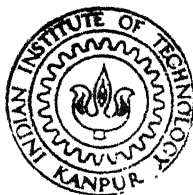


ENHANCEMENT OF ELECTRICAL CONDUCTIVITY IN ION-EXCHANGED OXIDE GLASSES

By
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MATERIALS SCIENCE PROGRAM
ADVANCED CENTRE FOR MATERIALS SCIENCE
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
DECEMBER, 1987

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**A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY**

**By
AVANISH KUMAR SRIVASTAVA**

**to the
MATERIALS SCIENCE PROGRAM
ADVANCED CENTRE FOR MATERIALS SCIENCE
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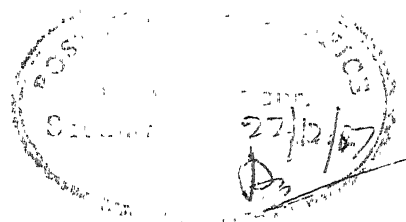
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*Dedicated to
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Parents*



CERTIFICATE

This is to certify that the thesis entitled 'ENHANCEMENT OF ELECTRICAL CONDUCTIVITY IN ION-EXCHANGED OXIDE GLASSES' by Avanish Kumar Srivastava is carried out under our supervision and has not been submitted elsewhere for a degree.

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Avanish
(AVANISH KUMAR SRIVASTAVA)

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ABSTRACT

The conductivity of glass is due to the mobility of certain ions within the structure. It is an electrolytic conductor. Alkali containing oxide glasses have long been known to conduct electricity by the alkali ion migration under the influence of an electric field. But only recently with the development of several high conducting glass systems, ionic conduction in glasses have attained new dimensions. Such glass systems are known as Fast Ion Conducting glasses (FIC) and they display very high value of ionic conductivity of the order of $10^{-2} \text{ (ohm cm)}^{-1}$ at room temperature. Highest conductivity is exhibited by FICs based on silver ion migration.

In the present thesis, work is based on the effect of sodium \rightleftharpoons copper and sodium \rightleftharpoons silver ion exchange treatment on electrical conduction in glasses.

Chapter 1 deals with electrical conductivity (both ionic and electronic) of glasses and literature survey along with AC and DC response of various glass systems and a brief review on FIC glasses.

Chapter 2 deals the experimental techniques used to prepare and characterize the glass-samples with different mole % of sodium. Procedure for ion-exchange treatment of

these glasses has been described. The characterization techniques include A.C. and D.C. electrical conductivity measurements, X-ray analysis, density measurement and Differential Scanning Calorimetry to get glass transition temperature of different glass samples.

Chapter 3 deals with AC and DC resistivities of certain glasses in bulk form based on the SiO_2 tetrahedral frame work with varying amounts of Na_2O (15-30 mole %). Ion-exchanged glasses show lowering of resistivity and activation energy values. An optimum combination of electrical field and temperature brings about a permanent morphological transformation in the ion-exchanged layer inducing a high conductivity state. The newly attained conducting state is characterized by activation energies tending to zero. It appears that the conduction in the newly formed state is ionic in nature.

Chapter 4 gives a summary of the results obtained in the present investigation.

CHAPTER 1

INTRODUCTION

Glasses are fused mixtures of various oxides and elements, they do not have uniquely fixed compositions and many thousands of glasses, each with a different composition, are produced commercially. If the melted mixture supercools, the volume decreases along the line bc and we get glassy state of matter, Fig. 1.1.

Glasses have a desirable range of electrical properties; they are cheap and they can be formed readily into complex shapes.

The soda-lime-silica glasses, which are mixtures of silica (SiO_2), sodium oxide (Na_2O) and calcium oxide (CaO) have long been known to conduct electricity by the sodium ion migration under the influence of an electric field. But only recently, ionic conductivity in glasses has received considerable attention because of the possible application of glasses as solid electrolytes (C. Tuller et al., 1980). It has been reported from sodium silver interdiffusion studies in oxide glasses that the activation energy for silver self diffusion as estimated from the interdiffusion coefficient values in these systems is small (Chakravorty et al., 1972). The silver-rich

layers produced by an ion-exchange reaction are usually only a few tens of micrometers thick (Collins et al., 1966). Similarly, we can carry out the ion exchange treatment using copper in place of silver.

The following sections give a brief review of the electrical properties and their mechanisms in glasses :

1.1 Electrical Properties of Glasses :

The conductivity of glass is due to mobility of certain ions within the structure: it is an electrolytic conductor. But the glasses exhibit a very wide range of specific resistivities at room temperature. The specific resistivities of glasses range from $10^{27} \Omega\text{-cm}$ (Calcium boro aluminate glasses) to $10^{-3} \Omega\text{-cm}$ (amorphous metallic alloys). In between these two are the oxide and chalcogenide semiconductors.

1.1.1 Electronic Conduction :

Three types of glass systems which show electronic conduction, are as follows :

1.1.1.1 Chalcogenide Glasses :

These glasses contain Group VI (Chalcogenide) elements, sulphur, selenium, and tellurium, alone or in combination with the group V elements; phosphorous, arsenic, antimony, and bismuth, and often including other elements such as thallium and

germanium. The glasses based on cadmium arsenide probably also belong in this category because of their similar behaviour. Their D.C. conductivity is given by

$$\sigma = \sigma_0 \exp (-E_0/KT) \quad (1.1)$$

where

E_0 - activation energy, which is a constant (Fritzsoche, 1974) usually in the range 0.5 to 1.0 eV

σ_0 - pre-exponential factor is of the order of $10^3 - 10^4$
 $(\Omega \text{ cm})^{-1}$

A.C. conductivity (in terms of variation of conductivity with frequency) is given by

$$\sigma(\omega) \propto \omega^n$$

where $0.7 \leq n \leq 1.0$.

1.1.1.2 Oxide Glasses Containing Transition Metal Ions :

The conductivity depends upon the concentration of transition metal oxide in the glass composition and the melting conditions, i.e., by melting temperature, the surrounding atmosphere and rate of cooling. The best known examples are the Vanadate glasses, such as $\text{BaO} \cdot 2\text{V}_2\text{O}_5$, $0.6\text{V}_2\text{O}_5 \cdot 0.4\text{Te}_2\text{O}$, and various vanadium phosphate glasses.

The conductivity for these glasses is given by (Mott 1968, Austin and Mott, 1969).

$$\sigma = \frac{\mu_{ph} e^2 C(1-C)}{KTR} \exp(-2\alpha_{\omega} R) \exp\left(-\frac{E_H + \frac{E_0}{2}}{KT}\right) \quad (1.2)$$

where

μ_{ph} - phonon frequency

α_{ω} - rate of decay of wave function of electrons at localized sites

C - ratio of concentration of ions in lower valency state and total concentration of transition-metal ions

R - average hopping distance

E_H - polaron hopping energy

E_0 - disorder energy.

1.1.1.3 Glass Metal Particulate Composites :

These type of glasses exhibit semiconductivity (Chakravorty 1984) and the effect is due to the tunneling of electrons from one metal grain to the next (Chakravorty et al., 1977). A theoretical model, to analyse the experimental results proposes, the generation of a charge carrier viz., electron. This involves creation of a pair of positively and negatively charged grains. The energy E_c^0 required to create such a pair is given by

$$E_c^0 = \frac{2e^2}{K_1 d} \quad (1.3)$$

where

e - electronic charge

d - metal grain diameter

$$K_1 = \xi \left[1 + \frac{d}{2S} \right]$$

ξ - dielectric constant of the glass matrix

S - interparticle separation.

Under certain approximations (Abeles 1976), conductivity is given by

$$\sigma = \sigma_0 \exp \left[-2 \left(\frac{C_1}{KT} \right)^{1/2} \right] \quad (1.4)$$

where

$$C_1 = X S E_c^0$$

$$X = \left[\frac{8\pi^2 m \Theta}{h^2} \right]^{1/2}$$

Θ - effective barrier height

m - electronic mass

h - Planck's constant.

1.1.1.4 Switching Behaviour :

Switching and 'memory' effects in glasses have been reviewed by Pearson and are discussed in many other papers,

especially the Journal of Noncrystalline Solids, Volumes 2,4 and 8 through 10. These effects have been found in Chalcogenide glasses, such as A_s-T_e (I, B_r, S_e), $A_s TlS_e$, $T_i A_s$ (S_e, T_e), and $A_s T_e S_i G_e$, in vanadium phosphates, in sodium borotitanate glass, in amorphous silicon and germanium in organic semiconductors, and probably occur in all semiconducting glasses.

Basically switching consists of a transition from a state of high resistance (OFF) to one of low resistance (ON), the transition being generated by the application of a specific voltage named threshold voltage V_{th} . Two types of processes are found i.e., threshold switching and memory switching. The difference lies in the fact that in the latter, once the current is suppressed, the state of low resistance remains. The explanation given for the ON state remaining when memory switching takes place is based on the presence of a crystalline filament which is a consequence of the Joule heating of the amorphous material

Two types of mechanisms which regulate switching have been proposed. One is based on effects of an electronic nature the other is founded on the consequences of the current flowing through the material .

1.2 Ionic Conduction in Glasses :

Various inorganic oxide glass systems like silicates, borates, phosphates and germenates exhibit ionic conductivity. The conductivity has Arrhenius like temperature dependence given by (Rawson 1984)

$$\sigma = \sigma_0 \exp(-Q/KT) \quad (1.5)$$

In a simple model where an ion is supposed to move in a periodic potential barrier of average height E , it can be shown that (Rawson H., 1984)

$$\sigma_0 = \frac{ne^2 \mu_c R^2}{2KT}$$

where

n - number of cations per unit volume

μ_c - vibration frequency of cation

R - average distance between adjacent sites.

Actually the Q and R denote some sort of average values, because the mobile ion in a glass experiences a potential barrier of random periodicity.

The general features of ionic conductivity in alkali containing oxides can be summarised as follows :

- (i) The ionic conductivity increases with increase of alkali oxide concentration but this increase is nonlinear.
- (ii) The activation energy decreases with increase in the alkali metal ion concentration.
- (iii) Conductivity is proportional to the square root of the alkali oxide activity in alkali silicates (Ravaine and Souquet 1973, 1977, 1978).

1.2.1 Fast Ion Conduction

Recent advances in the development of fast ion conducting glasses (FIC) have opened up many new applications including high energy density batteries, electrochromic displays and sensors. Most of such FIC glasses are based on compositions derived from silver iodide. Many basic features which have been revealed for these FIC's are as follows :

- (i) They are formed in glass systems which are known to involve considerable network structures like silicate, phosphate and borate systems and in molybdate and halide systems where bonding is essentially ionic.
- (ii) Preexponential factor σ_0 is much smaller in case of FIC's than that for normal ionic conductors.

- (iii) Q for Ag^+ FIC's lie in the range of .15 to .47 eV while Q for Li^+ FIC's lie in the range of .31 to .73 eV (Kulkarni, 1984).
- (iv) AgI which is the component of several glass FIC's is itself a fast ion conductor in its (high temperature) crystalline form.

There are two theories for conduction process in FIC glasses :

1. Random site model : All ions of the particular type are treated as potential carriers with a Gaussian distribution of activation energy and the mobility varies with the distribution of activation energy and thereby with the glass composition. In general the variation of carrier concentration is relatively small and thus the change in conductivity with composition is mainly controlled by the change in mobility.
2. Weak electrolyte model: A fraction of the total ions of that type contribute to the conduction, the rest remaining immobile, while the mobility is independent of glass composition.

1.2.2 AC Electrical Properties of Oxide Glasses :

Polarisation of an insulator under an electric field is due to the displacement of several kinds of charges. Polarisation varies with time as shown in Fig. 1.2 and can be

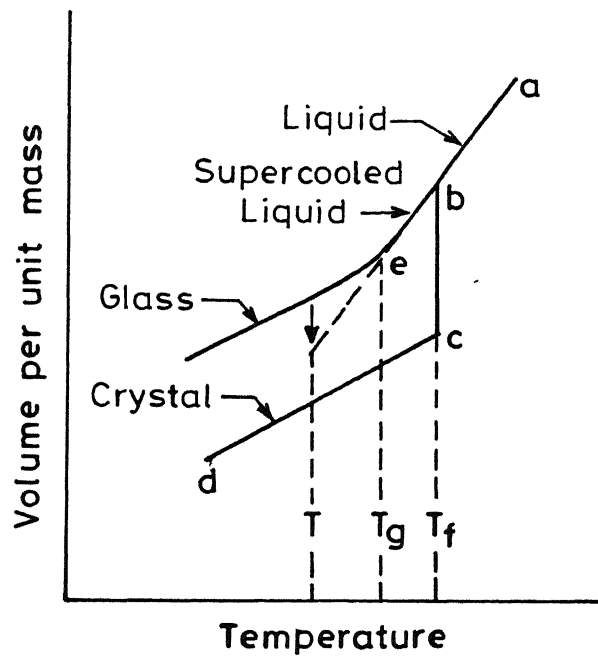


Fig.1.1 Relation between the glassy, liquid and solid states.

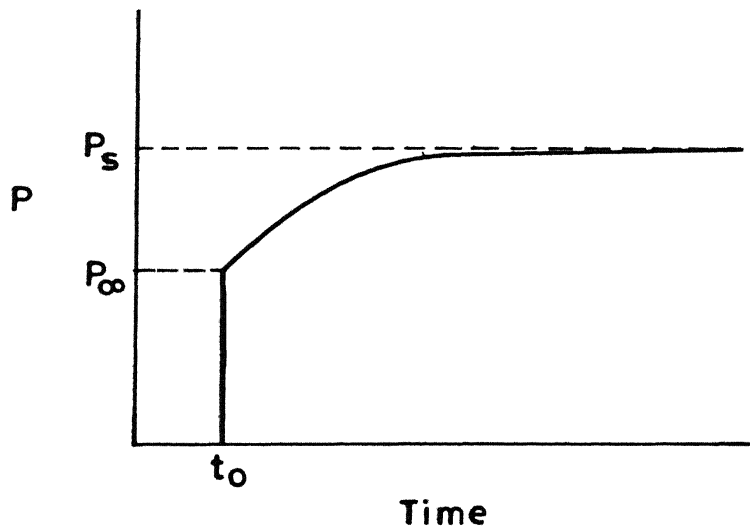


Fig. 1.2 Time dependence of polarisation after applying a constant D.C. field at time t_0 .

represented as

$$P(t) = (P_s - P_\infty) \left[1 - \exp\left(-\frac{t - t_0}{\tau}\right) \right] \quad (1.6)$$

where

τ - relaxation time

P_s - polarisation at time $t = \infty$

P_∞ - initial value of polarisation

As the temperature increases, the decreases

$$\tau = \tau_0 \exp(E / KT)$$

E_τ - activation energy for the relaxation.

If the field alternates, there may be insufficient time in one half cycle for ions to reach their final positions and for polarisation to reach the final value P_s . At very high frequencies none of the ions may move in one half cycle and the polarisation will then not exceed the instantaneous value P_∞ .

If a glass is subjected to a periodic electric field, there will generally occur a phase angle ϕ which shows how much the difference in phase between current and applied voltage differs from $\pi/2$. The angle ϕ is termed as loss angle and $\tan \phi$ the dissipation factor.

Power dissipated in the form of heat (ω) per unit volume per unit time is given by

$$\omega = \frac{E_o^2 f \epsilon' \tan \delta}{8\pi} \quad (1.7)$$

The conduction loss depends on the resistivity ρ and is given by

$$\tan \delta = \frac{1}{2\pi f \epsilon' \epsilon_o \rho} \quad (1.8)$$

where

E_o - maximum value of electric field strength

f - frequency of applied field

ϵ' - dielectric constant at the given frequency

$\epsilon_o = 8.85 \times 10^{-14}$ F/cm if ρ is expressed in Ω cm

$\epsilon' \tan \delta$ - loss factor, is a measure of dielectric losses
AC conductivity is given by

$$\sigma_{AC} = 2\pi f \epsilon_o \epsilon' \tan \delta \quad (1.9)$$

1.2.3 Electrode Polarization

Ion transport within a glass under a DC potential eventually leads to a build up of charge at the glass, electrode interface if the ions are not replenished at the electrode (i.e., if the electrodes are blocking). As a result conductivity

decreases with time. The reason is that the mobile cations pile up at the electrodes which results in an induced back field. The back field concentrates the potential drop in the electrode region. Since the potential across the bulk of the sample is decreased to a fraction of the applied voltage the force on the mobile ions in the bulk decreases. The back field builds up indefinitely with time resulting in a continuous decrease in glass conductivity with time.

1.3 Ion Exchange :

When a glass containing monovalent cations is placed in a medium having another type of monovalent cations, such as a fused salt or aqueous solution, these cations can exchange with the monovalent cations in the glass matrix and inter-diffuse. When a glass is ion-exchanged by silver or copper ions is carried out about the glass transition. Temperature T_g , the network of glass adjusts itself to the differing partial molar volumes of the exchanging ions when the temperature is less than T_g , it results in stress in the glass. If the salt bath ions are larger than the host ions in the glass, there is a resultant compression which increases the strength of the glass.

The general expression for diffusivity

$$C(x,t) = A - B \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right)$$

where

$C(x,t)$ - concentration of ions at the distance x and time t

A and B - constants

erf . - error function

D - diffusion coefficient of ions for the matrix.
It is dependant on temperature.

An exchanging cation normally has a mobility different from that of the original ion therefore as interdiffusion proceeds one ion tends to outrun the other and an electrical potential is built up. However, accompanying this change is a potential gradient that slows down the fast ions and speeds the slow one. To preserve charge neutrality the fluxes of the two ions should be equal and opposite and the potential gradient ensures this inspite of the difference in the mobility of the cations.

1.4 Objectives of Present Investigation

Some recent work in this laboratory has shown that high electrical conductivity can be induced in certain oxide glasses

by subjecting them to a sodium silver ion exchange treatment. Alkali containing glass fibres, under ordinary conditions of ion exchange viz., temperature around 325 °C and duration extending to 50 hours, show the resistance of the order of few ohms in the high conducting state [D. Chakravorty and A. Shrivastava 1986]. As a logical extension of these results the present investigation is carried out.

- 1) To prepare the alkali containing glasses of different compositions.
- 2) To show the effect is valid in bulk glasses also in the $\text{Na}^+ \rightleftharpoons \text{Ag}^+$ exchange case.
- 3) To explore the effect of $\text{Na}^+ \rightleftharpoons \text{Cu}^+$ exchange on the electrical properties of alkali containing glasses.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

In this chapter various aspects of preparation of glasses in bulk form and the method for measuring their different properties are discussed. Different compositions of the glasses investigated are given in Table 3.1.

2.1 Preparation of Glass :

The glasses, presented in Table 3.1, are prepared from reagent grade chemicals. Na_2O is introduced as sodium carbonate, CaO as calcium carbonate, B_2O_3 as boric acid and other ingredients (SiO_2) as their respective oxides. Each glass batch of a given composition is weighed, mixed thoroughly using acetone as grinding medium in FRITSCH Ball Mill. Each mixture is dried and melted in pure alumina crucible in a temperature controlled electrically heated furnace, in the range of 1200°C to 1450°C . The glass melt is kept at this temperature for about 2 hours and is mechanically stirred so as to make it bubble free and homogeneous. The melt is poured into an aluminium mould to get a rectangular glass block which is immediately taken inside an annealing furnace maintained at 500°C where it is annealed for about 6 hours. After taking it out from the annealing furnace, it is kept inside a desiccator.

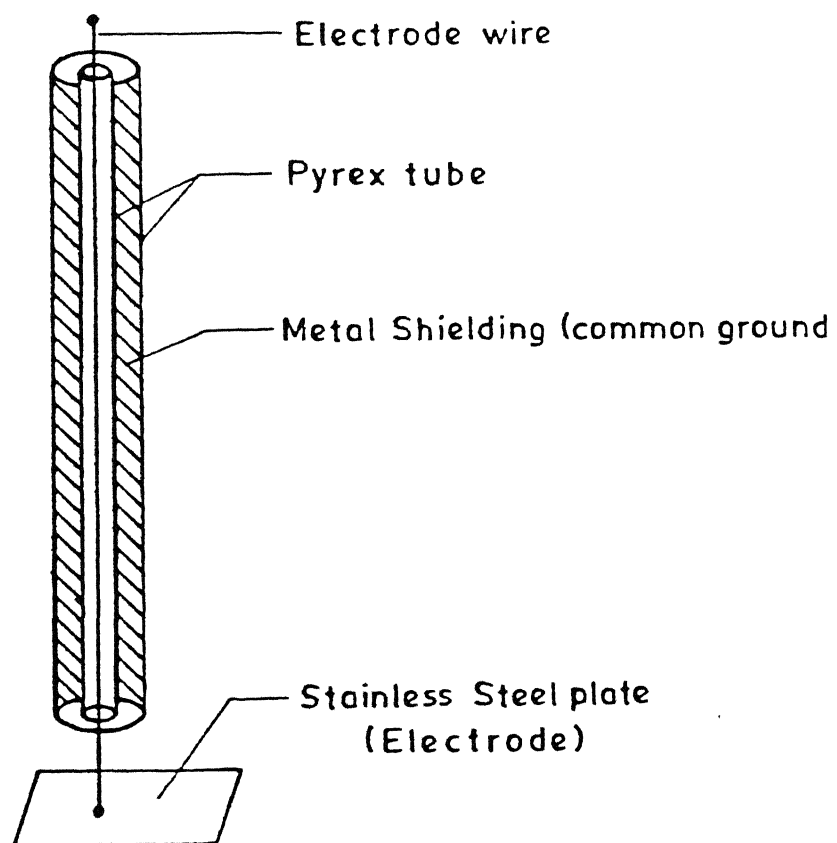
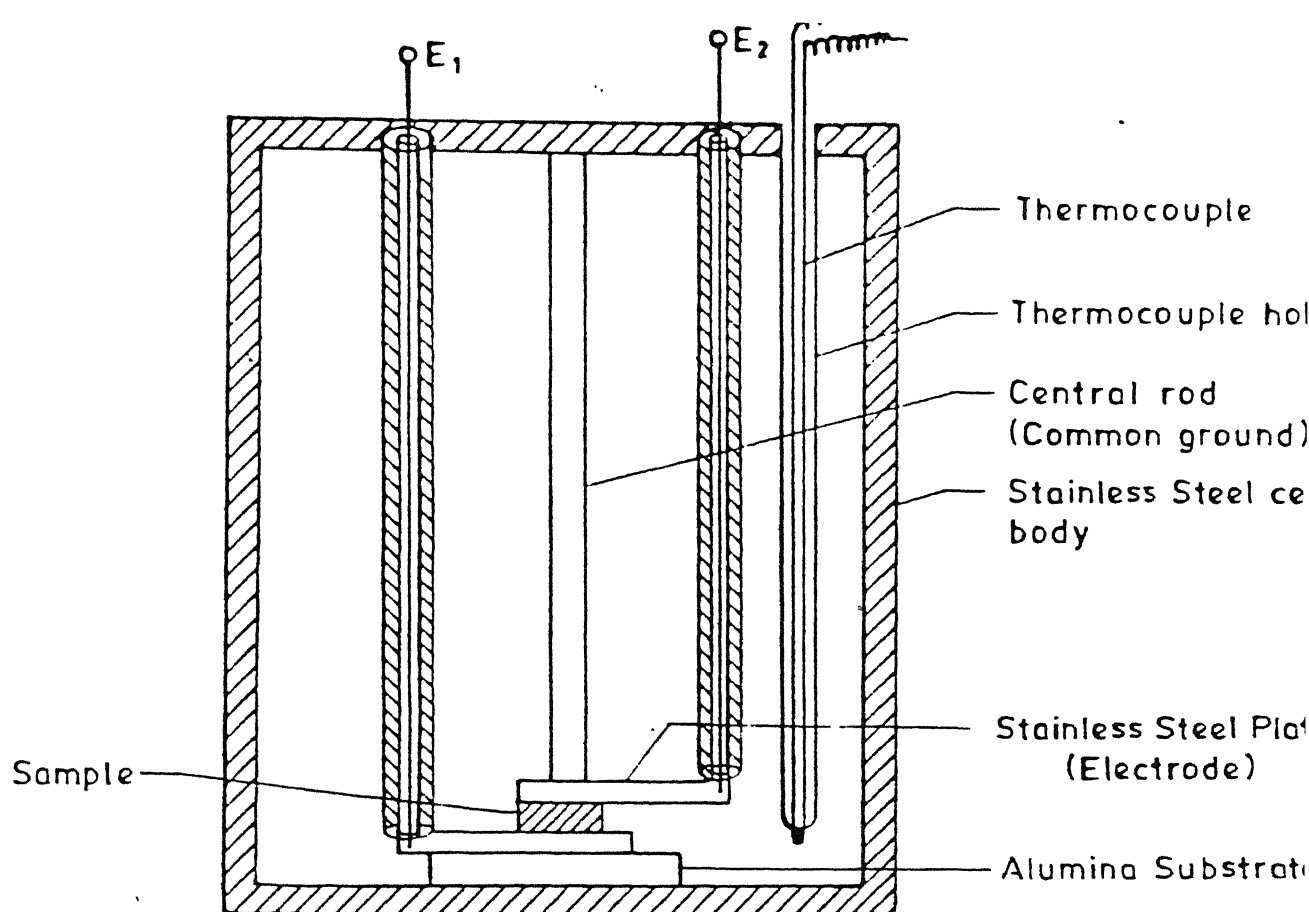


Fig. 2.1 Schematic view of the conductivity cell.

2.2 Sample Preparation for Electrical Resistivity Measurement :

The sample is prepared by polishing the glass piece using silicon carbide grit of different mesh sizes (100, 240, 320, 400, 600, 800 respectively) to the dimensions approximately 5 mm x 5 mm x 2 mm (for measurements on virgin glass sample) and 3 mm x 3 mm x 1.5 mm (for preparing ion-exchanged glass samples).

2.2.1 Ion Exchange :

In order to produce ion-exchanged glass samples the glasses kept in a molten bath of silver nitrate (for $\text{Na}^+ \rightleftharpoons \text{Ag}^+$ ion exchange) and cuprous chloride (for $\text{Na}^+ \rightleftharpoons \text{Cu}^+$ ion exchange). In this process the sodium ions are exchanged by the copper ions (in $\text{Na}^+ \rightleftharpoons \text{Cu}^+$ ion exchange) and silver ions (in $\text{Na}^+ \rightleftharpoons \text{Ag}^+$ ion exchange) in the glass sample upto a certain thickness.

2.2.1.1 $\text{Na}^+ \rightleftharpoons \text{Cu}^+$ ion Exchange

The sample is kept in a silica boat containing molten CuCl at 525°C in an electrically heated furnace for two different timings (to get two hours and twelve hours ion-exchanged samples). The treatment is carried out under an argon gas atmosphere. After the ion exchange treatment is over, the boat is taken out from the CuCl melt. These samples are treated in dilute nitric acid for 15 minute's duration

and then washed thoroughly in water and acetone respectively to remove any CuCl adhering to their surfaces.

2.2.1.2 $\text{Na}^+ \rightleftharpoons \text{Ag}^+$ ion Exchange

The sample is kept in a pyrex boat containing molten AgNO_3 at 330°C in an electrically heated furnace for 48 hours. After the ion-exchange is over, the sample is taken out. These samples are treated in boiling water for 2 hour duration and then washed in running water to remove any excess AgNO_3 , adhering to the sample surfaces.

2.2.2 Electrode Preparation :

Thin layers of silver paint are applied on two opposite surfaces of the larger dimensions after measuring the cross-sectional area and thickness of both virgin as well as ion-exchanged glass samples.

2.3 Conductivity Cell :

Figure 2.1 shows the schematic view of the cell used for electrical measurements. It consists of a stainless steel tube of about 300 mm length and of 50 mm diameter. The tube has a cooling coil assembly attached to its top. The main structure i.e., the sample holder can be fitted within this jacket.

The main structure of the cell consists of two stainless steel rods fixed to a bronze flange which act as two electrodes (E_1 and E_2). Each rod is brazed to a rectangular stainless steel plate so that the sample can be sandwiched between the two plates. Both the electrodes have spring arrangements so that they can be moved up and down. The lower electrode is supported on an alumina substrate which itself is attached rigidly to the main structure. A chromel-alumel thermo-couple is placed near the electrode assembly, its other end is taken out through the teflon disc fitted into the flange. There is a control rod in the main structure which can be connected to ground. Also the electrodes are shielded by (Fig. 2.1) metal shielding. By this set up the temperature can be varied from room temperature to 500°C with an accuracy of $\pm 1^{\circ}\text{K}$. The temperature is controlled by a temperature controller (Indo-therm Model DTC-120).

2.4 Electrical Resistivity Measurement :

The d.c. resistivity of silicate glasses ranges from 10^{15} to $10^{-2} \Omega \text{ cm}$ depending on the composition and temperature. For many glasses, particularly at low temperatures, the initial current which flows immediately after the application of an electric field is much larger than the eventual steady state current. This anomalous conductivity can persist

for many minutes and even hours. The existence of this transient conductivity does complicate the measurement of resistance, since polarization of the electrodes cannot be avoided by using low frequency a.c. voltages. The a.c. conductivity of a glass is often significantly greater than the true d.c. conductivity because the former includes a contribution from the anomalous current. That is why, we are concerned with the measurement of a.c. resistivity also, especially at low temperatures.

2.4.1 D.C. Resistivity :

Figure 3.2 represents the schematic diagram of circuit used for measurement of current-voltage characteristics of different samples. The sample and the standard resistance are in series with a 30 V 2 amp. DC regulated power supply (APLAB Model 7152). The potential drop across the standard resistance is fed to Y axis of XY recorder (No. 2000 made by Digital Electronics Ltd., India). The potential drop across the sample is fed to Keithley Electrometer (Model 610) whose output is fed to the X axis of the XY recorder. Use of electrometer is necessary because of the impedance mismatch of sample ($\approx 10^{10} \Omega$) with that of the XY recorder ($10^6 \Omega$). The applied voltage is varied by the power supply and the potentiometer connected across it and this is recorded as I-V

characteristic on the X-Y recorder at a given temperature.

If R is the resistance determined by the slope of I-V curve at a given temperature, then resistivity, ρ is given by

$$\rho = R \cdot \frac{A}{l}$$

A - area of cross-section of the electrode

l - thickness of sample.

Before each measurement, the temperature of the system is maintained constant for sufficient time to attain the equilibrium by the arrangements described earlier.

2.4.2 A.C. Resistivity : Complex Impedance Analysis A.C. Data:

The schematic circuit diagram for A.C. resistivity measurement is given in Fig. 2.2. A General Radio GR 1615 transformer ratio arm capacitance bridge with GR 13136 oscillator bench and GR 1232 tuned amplifier and null detector are used to measure capacitance C and loss factor $\tan \delta$ at various frequencies (0.3, 0.5, 1.0, 3.0, 5.0, 7.0, 10.0, 15.0, 20.0, 50.0 and 100 kHz respectively) and at various temperatures (ranging from room temperature to 250 °C).

The real and imaginary parts of the complex impedance can be calculated by using the values of $\tan \delta$ and the capacitance

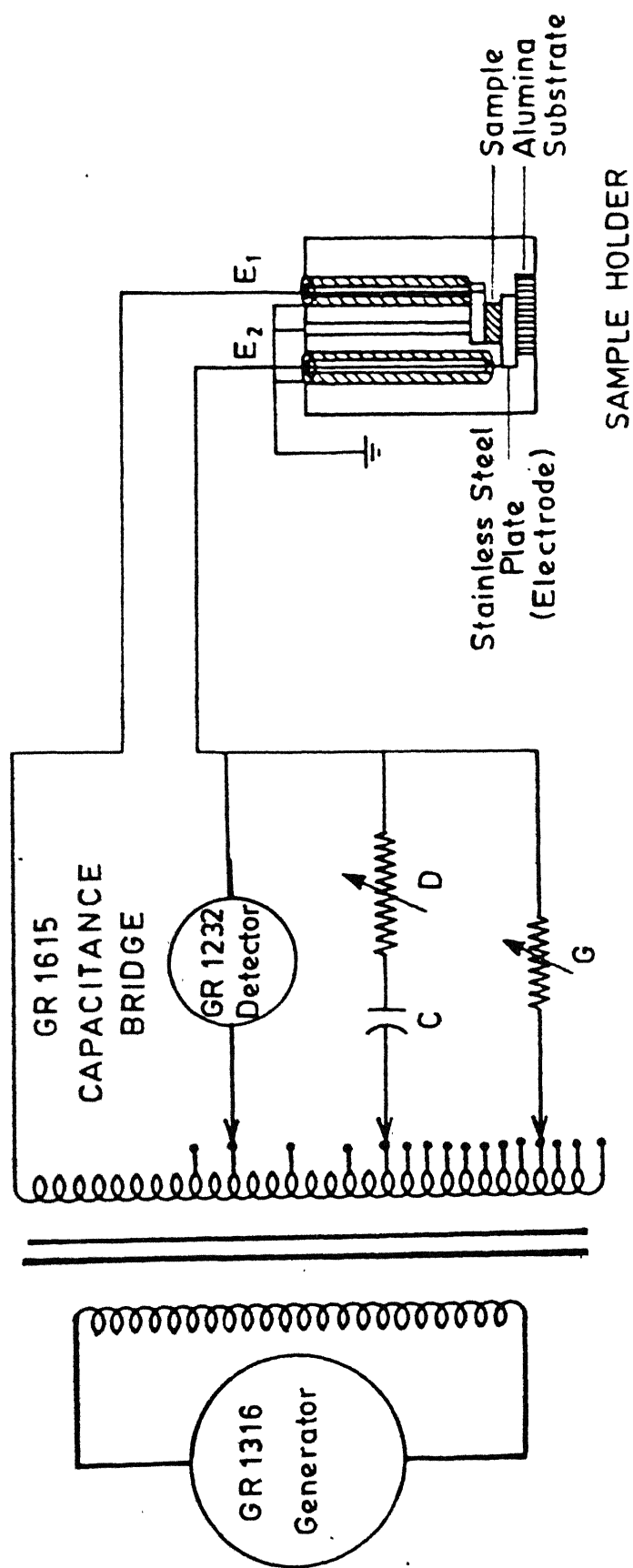


Fig. 2.2 Schematic circuit diagram for A.C. resistivity measurement.

$C(\omega)$. The complex impedance is given by

$$Z^* = Z' - iZ'' = \frac{G}{G^2 + \omega^2 C^2} - i \frac{\omega C}{G^2 + \omega^2 C^2} \quad (2.1)$$

Hence,
$$Z' = \frac{G}{G^2 + \omega^2 C^2} \quad (2.2)$$

and

$$Z'' = \frac{\omega C}{G^2 + \omega^2 C^2} \quad (2.3)$$

where G is the conductance and $G = \omega C \tan \delta$ (2.4)

The capacitance and $\tan \delta$ values are measured at various frequencies and for various temperatures and the values of Z' and Z'' are calculated using above equations. Complex impedance plots are made from these data. The plot is usually a semicircle passing through the origin. The intersection of the plot on the Z' axis gives the value of dc resistance at the particular temperature.

2.5 X-Ray Analysis :

The virgin glass samples are ground to a very fine powder. 'Rich Seifert 2002D Isodebyeflex Diffractometer' with a beam of $\text{CuK}\alpha$ (wavelength = 0.291 nm) radiation has been used to record the X-ray diffraction pattern of the glass samples at the scanning speed of 3° per minute.

2.6 Differential Scanning Calorimetry (D.S.C.) :

A Dupont 910 DSC is used for thermal analysis of the powder sample of different glass compositions. The powdered samples is put in small aluminium pan provided by the manufacturer to use as crucible. A second empty Al pan is used as a reference. The heating cycle in the D.S.C. for example, the initial temperature, final temperature, rate of heating, minutes in isothermal etc. are programmed. The specimen is heated from 50 °C at a rate of 5 °C per minute to the final temperature of 580 °C. On the D.S.C. and the recorder system measurements can be made in different sensitivities.

Two sensitivity ranges 1x and 10x are available in D.S.C. The chart recorder sensitivity can be chosen from 0.01 and 100 volt full scale reading. For the experiment 1x D.S.C. sensitivity and 0.1 volt chart recorder sensitivity are used. The measurements are made in D.S.C. calibrated mode of the equipment. Base line adjustments are made at the start of the set of experiments but no adjustments are made in between to avoid the change in D.S.C. peak characteristic. The two-pen change recorder is used to record against time, Q, Q being the heat-evolved or absorbed and T, the temperature. The typical experimental conditions used are shown as below :

Heating rate	= 5 °C/min.
Initial temperature	= 50 °C
Final temperature	= 580 °C
Range for Q	= 0.1 V
Range for T	= 0.1 V
D.S.C. Sensitivity	= 1x
D.S.C. in calibrated mode.	

2.7 Density Measurement :

Density of glass is measured by the bouyancy method. A known weight W_1 of glass is dipped into the Toluene and weighed giving its value W_2 . Density is calculated by following formulae,

$$d_G = \frac{W_1}{W_1 - W_2} d_T$$

where

d_T - density of Toluene = 0.861 gm/cc

d_G - density of glass.

2.8 Regression of Line :

We know that the ionic resistivity of alkali-containing glasses as a function of temperature shows a temperature variation given by :

$$\rho = \rho_0 \exp \frac{Q}{KT} \quad (2.5)$$

where

Q - activation energy, which is a constant.

ρ_0 - pre-exponential factor

K - Boltzman constant

ρ - resistivity of the given sample at the temperature T

The plot of $\log(\rho)$ vs. $\frac{1}{T}$ should therefore be a straight line and the value of activation energy can be calculated from the slope of such a line. We can calculate the activation energy and pre-exponential factor more precisely, by using the 'Principles of Least Squares', with the minimum \pm error.

Taking logarithm on both the sides of $\rho = \rho_0 \exp \frac{Q}{KT}$

$$\log \rho = \log \rho_0 + (Q/K) \frac{1}{T} \quad (2.6)$$

or

$$Y = C + m X \quad (2.7)$$

where $\log \rho = Y$, $X = 1/T$, $Q/K = m$ and $\log \rho_0 = C$.

Condition of least square fit for the straight line gives

$$m = \frac{\bar{X} \cdot \bar{Y} - \bar{X} \bar{Y}}{(\bar{X})^2 - (\bar{X}^2)} = \text{slope of line} \quad (2.8)$$

and

$$C = \frac{\bar{X} \cdot \bar{X} \bar{Y} - \bar{Y} \cdot \bar{X}^2}{(\bar{X})^2 - (\bar{X}^2)} = \text{Intercept of line on Y-axis} \quad (2.9)$$

\bar{X} , \bar{Y} are mean values of X and Y variables respectively.

$$\text{Var}(m) = \frac{F_K^2}{[\sum X_i^2 - n(\bar{X})^2]}$$

$$\text{Var}(C) = F_K^2 \left[\frac{1}{n} + \frac{\bar{X}^2}{[\sum X_i^2 - n(\bar{X})^2]} \right]$$

where

$$\begin{aligned} F_K^2 &= \frac{1}{n-2} [\sum (Y_i - C - mX_i)^2] \\ &= \frac{1}{n-2} [\sum Y_i^2 - n\bar{Y}^2 - \frac{(\sum X_i Y_i - n\bar{X}\bar{Y})^2}{(\sum X_i^2 - n\bar{X}^2)}] \end{aligned}$$

The evaluated m and C lies between $m \pm m$ and $C \pm C$ respectively such that

$$m = \sqrt{\text{var}(m)}$$

$$C = \sqrt{\text{var}(C)}$$

2.9 Polarization Measurements :

Wagher's asymmetric polarization cell technique has been used in this investigation to determine the conductivity of glassy electrolyte in the high conducting state. Silver paint served as the reversible electrode whereas graphite paint (Polaron Equipment Ltd., England) served as the blocking electrode.

The cell Ag/High conducting glass system/ $C^{(+)}$ is clamped in the sample holder. The temperature of the furnace is raised and maintained at a constant temperature for 30 minutes before polarizing the cell. Small polarizing voltages are applied by a potentiostat and the polarizing current is monitored. For each of the voltages the steady-state current is recorded, in each case until there is an abrupt rise of current.

CHAPTER 3

RESULTS AND DISCUSSION

The virgin glass specimens which have been investigated are referred to as glass system A. Table 3.1 gives the composition of these glass systems. The ion-exchanged glass samples are being referred to as IA glass system and the high conducting glass samples are referred to as HIA glass systems.

3.1 Ion Exchange :

Samples for ion exchange treatment are prepared as given in Section 2.2.1. After ion exchange the thickness of silver rich layers and copper rich layers are usually only a few tens of micrometers thick (Collins et al. 1966). The morphology of the ion exchanged sample can be represented schematically as shown in Fig. 3.1.

3.2 X-ray Analysis :

Fig. 3.3 gives the X-ray analysis for different glass compositions. A broad peak is found in each plot which is characteristic of an amorphous material.

3.3 Density of the Glasses

The densities of the different glass samples have been

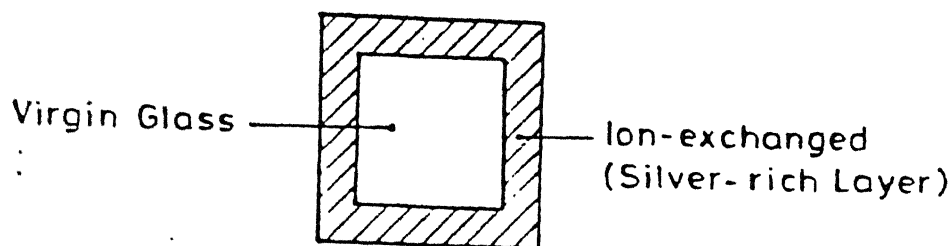


Fig. 3.1 Schematic representation of the morphology of ion-exchanged sample.

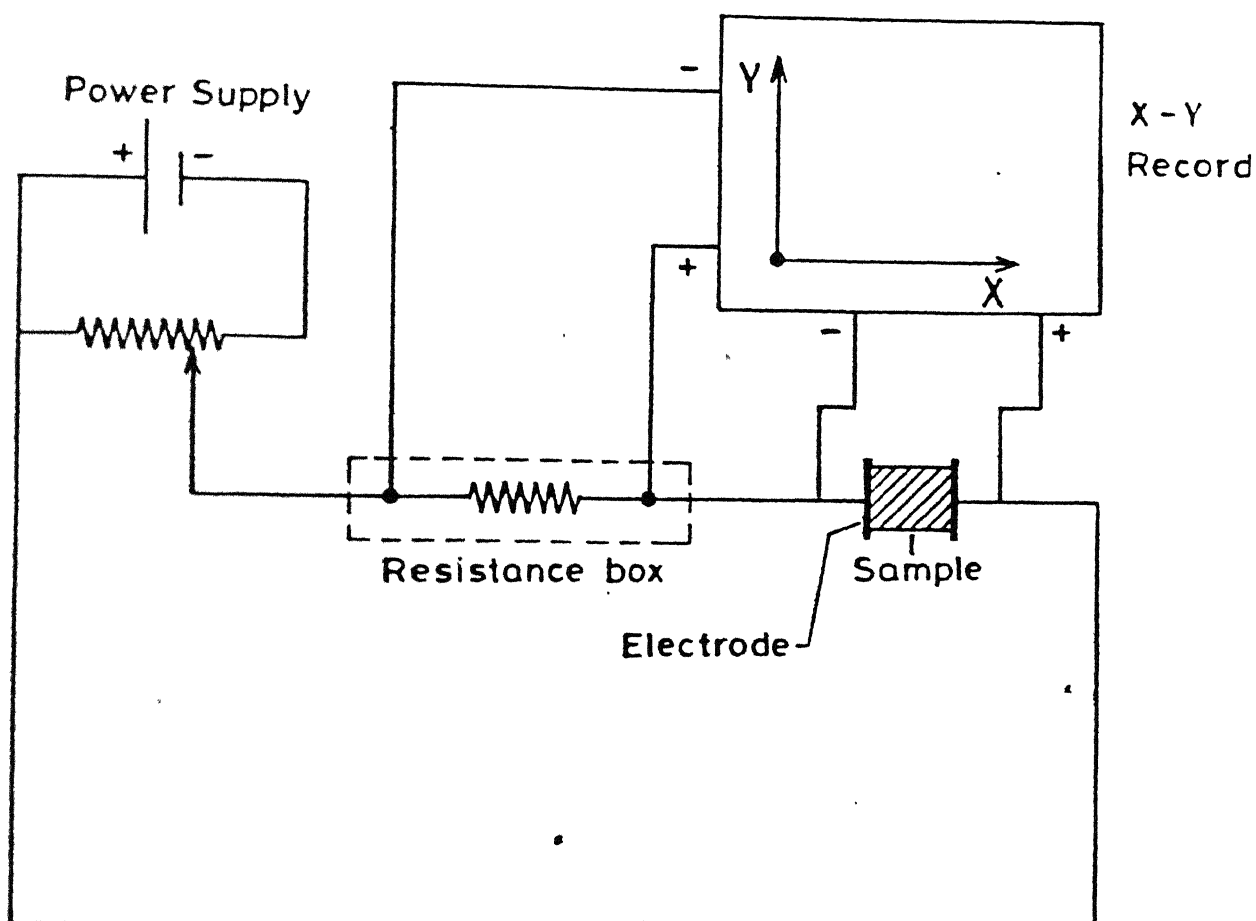


Fig. 3.2 Schematic circuit diagram for DC Resistivity measurements.

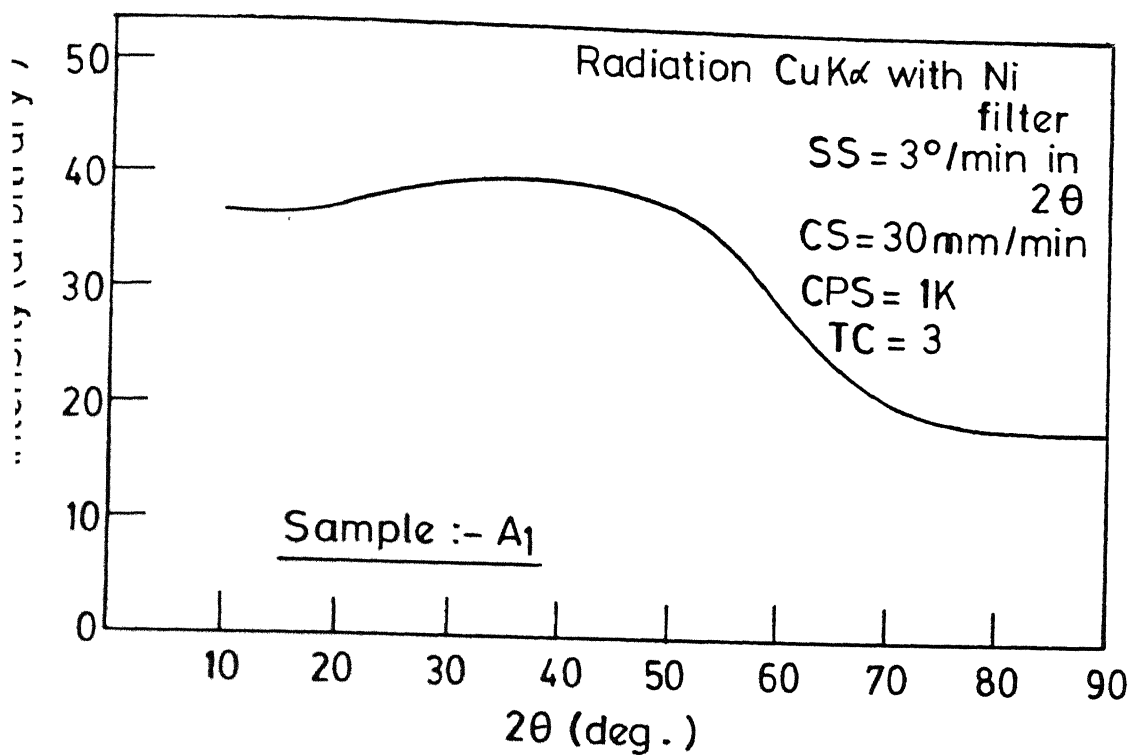


FIG. 3.3 a

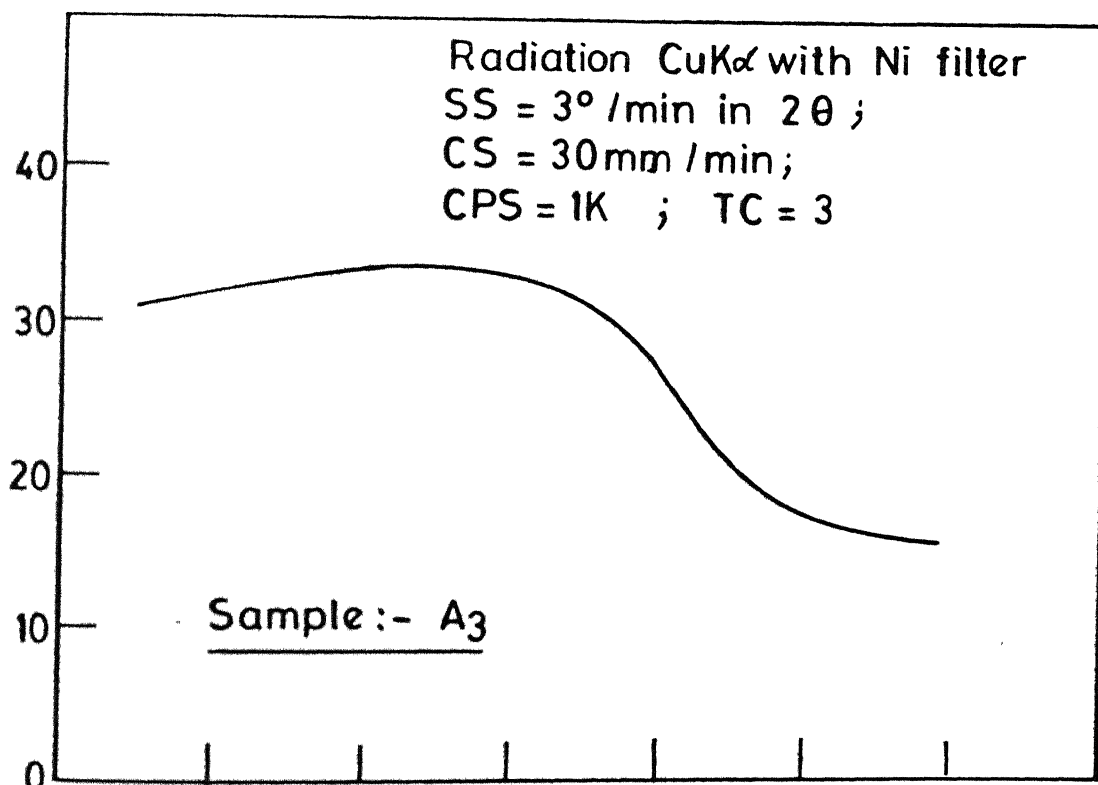


Table 3.1 Composition of the Glasses

No.	Glass system	Mole %				
		Na_2O	CaO	B_2O_3	Al_2O_3	SiO_2
A_1		15.0	13.0	8.0	4.0	60.0
A_2		20.0	13.0	4.0	3.0	60.0
A_3		25.0	13.0	4.0	3.0	55.0
A_4		30.0	12.0		3.0	55.0
A_5		20.0		66.0	14.0	

measured by liquid displacement method. The values are given in Table 3.2.

3.4 Differential Scanning Calorimetry :

Figure 3.4 gives the Q versus T plots for different glass samples. The value of glass transition temperature have been found out and is given in Table 3.2.

3.5 Electrical Measurements :

A.C. and D.C. resistivity measurements for the glass systems have been carried out as discussed in Sections 2.4.2 and 2.4.1. I-V plots are obtained on X-Y recorder by the circuit described in Section 2.4.1. The slopes of these curves give DC resistance of the sample.

3.5.1 A.C. Measurements and Complex Impedance Analysis :

A.C. measurements yield the values for conductance (G) and capacitance (C) as a function of frequency. As discussed in Section 2.4.2, the real (Z') and imaginary (Z'') parts of impedance are calculated by equations (3.1) and (3.2)

$$Z' = \frac{G}{G^2 + \omega^2 C^2} \quad (3.1)$$

$$Z'' = \frac{\omega C}{G^2 + \omega^2 C^2} \quad (3.2)$$

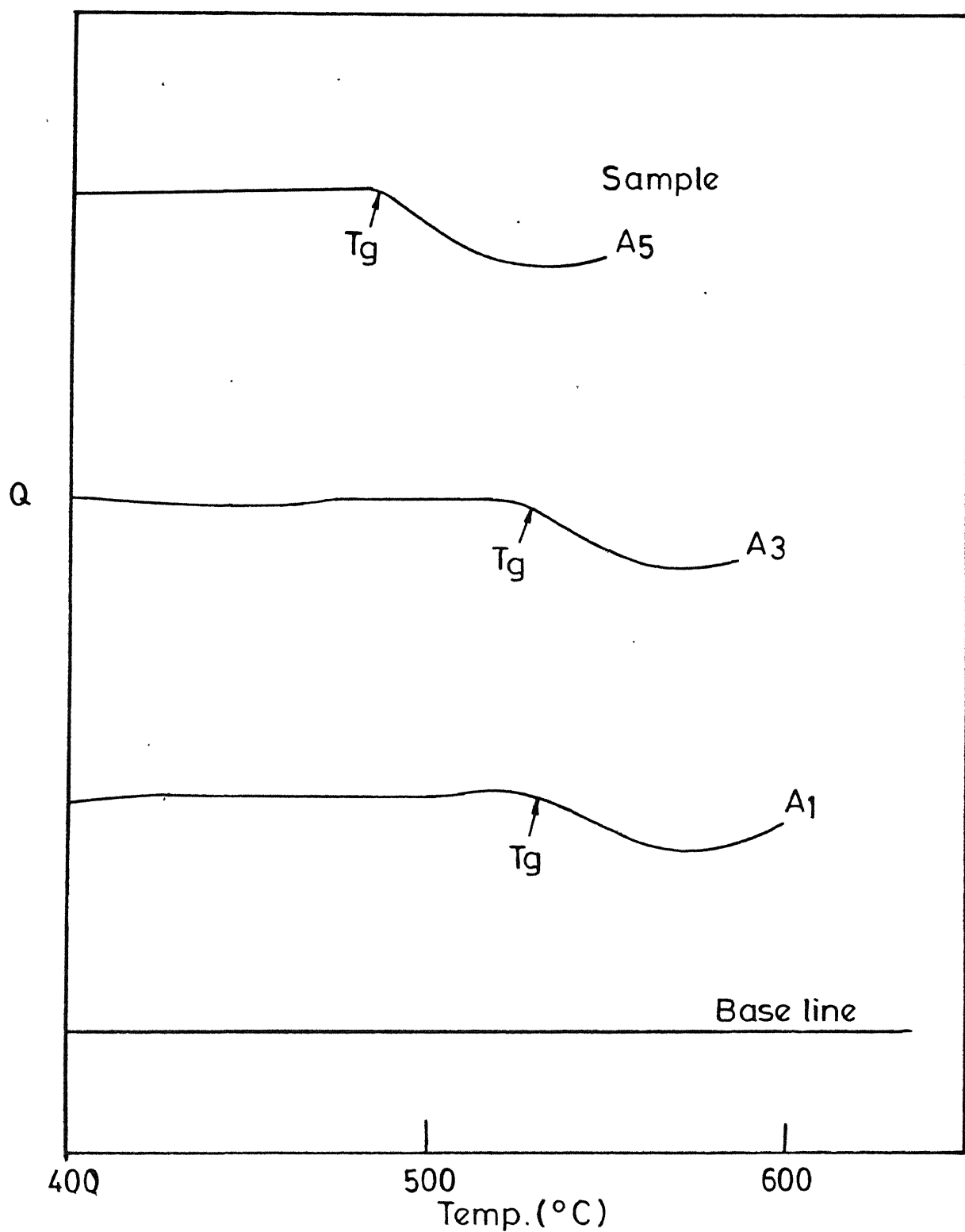


FIG. 3.4 DIFFERENTIAL SCANNING CALORIMETRY FOR DIFFERENT GLASS SAMPLES

Table 3.2 Density and Glass Transition Temperature (T_g)

S.No.	Glass system	Density (g/cc)	T_g °C
1	A ₁	2.713	530
2	A ₂	2.605	552
3	A ₃	2.624	529
4	A ₄	2.580	528
5	A ₅	2.793	490

Various points in the Z'' - Z' plane are found to lie on the arc of a semicircle passing through the origin, the centre lying on the X-axis. The intersection of this arc on the real (Z') axis other than the point of intersection at the origin yields the D.C. resistance R_{dc} of the sample. Figs. 3.5 to 3.19 are typical Z'' - Z' plots for the different virgin and ion-exchanged glass systems.

3.6 Temperature Dependence of Resistivity :

Resistivity of various glass samples have been calculated from the complex impedance plot for various temperatures in the range of room temperature to 250 °C for the virgin glass systems and ion-exchanged glass systems.

It has been found that ion-exchanged glass (IA) samples invariably show a sudden surge of current when the applied electric field E exceeds a critical value E_c . The value of the critical field E_c is dependent upon the temperature (T_c) for a given glass composition. Thus an optimum combination of electric field and temperature brings about a permanent change in the resistivity of these glass systems. The newly attained state has resistivities many orders of magnitude lower than that of the ion-exchanged glass systems. Once the ion-exchanged glass system attains this high conducting state it is being referred to as HIA glass system.

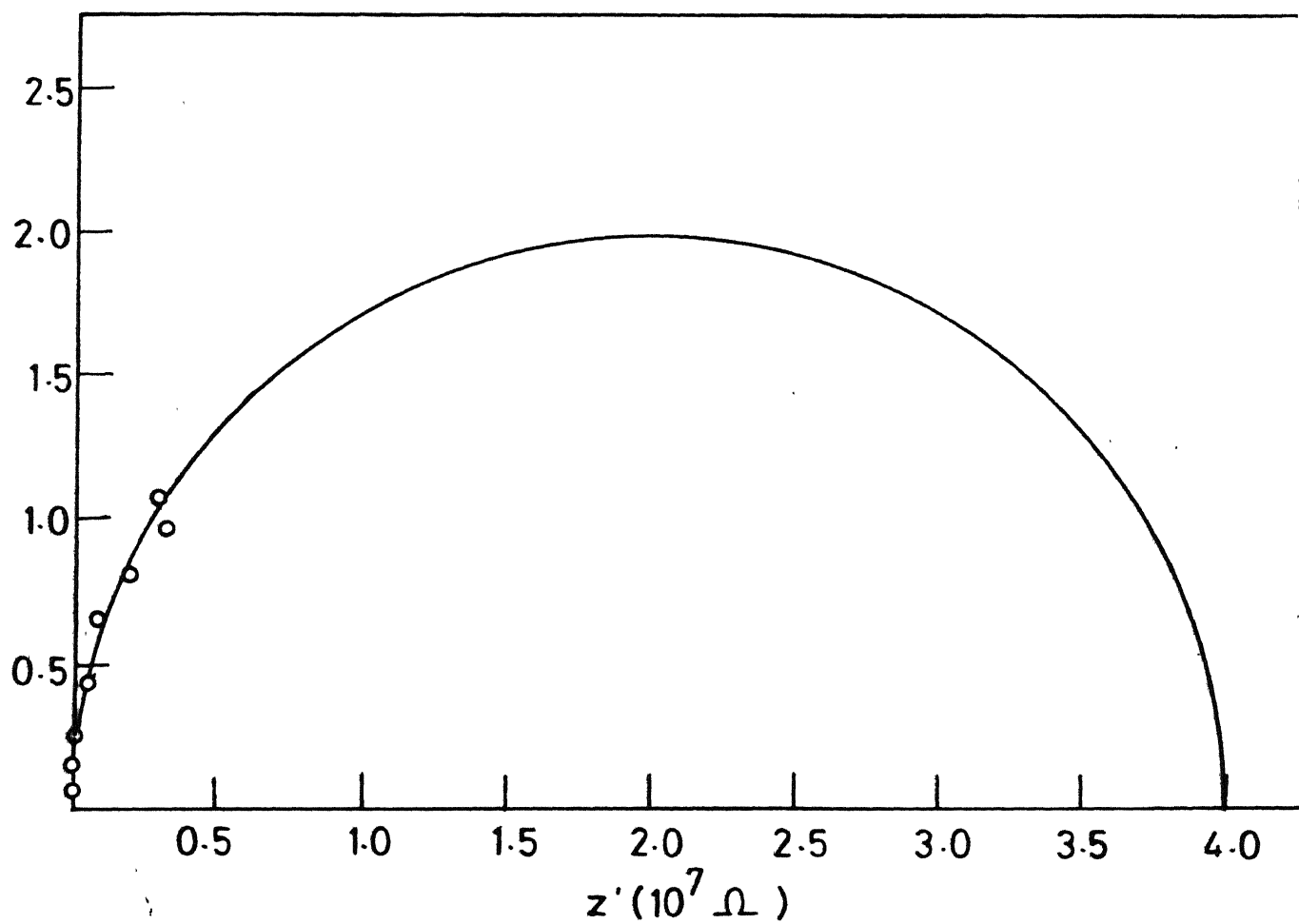


FIG.3.5 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM A₁
($T = 200^\circ\text{C}$)

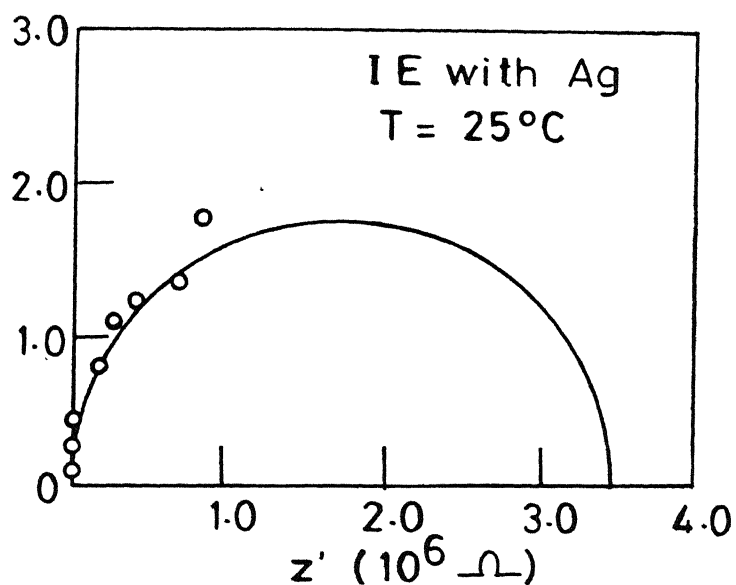


FIG. 3.6

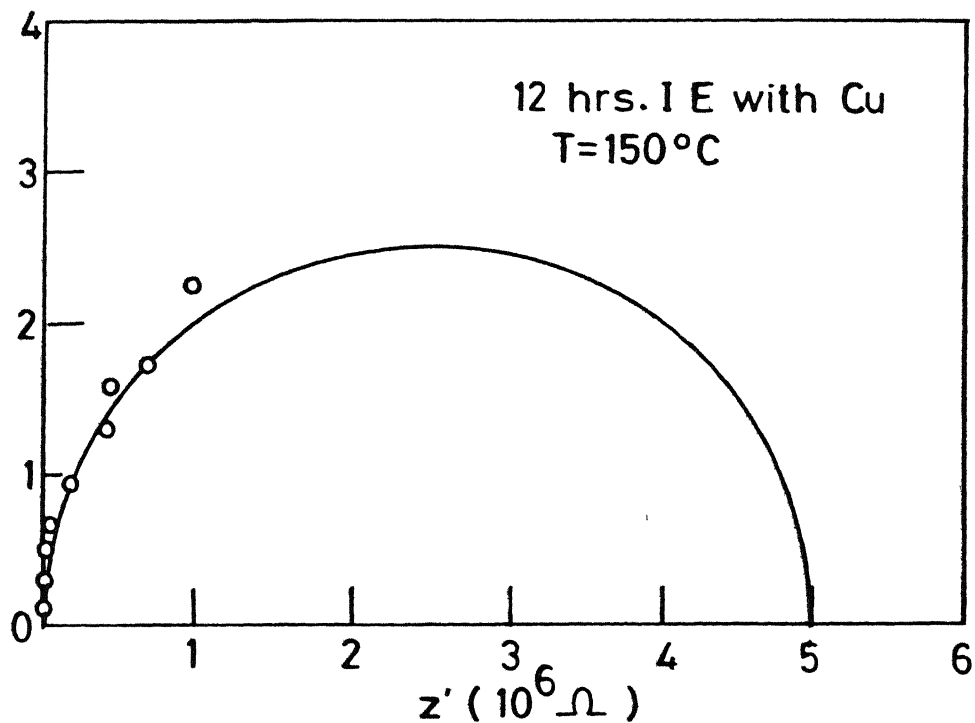
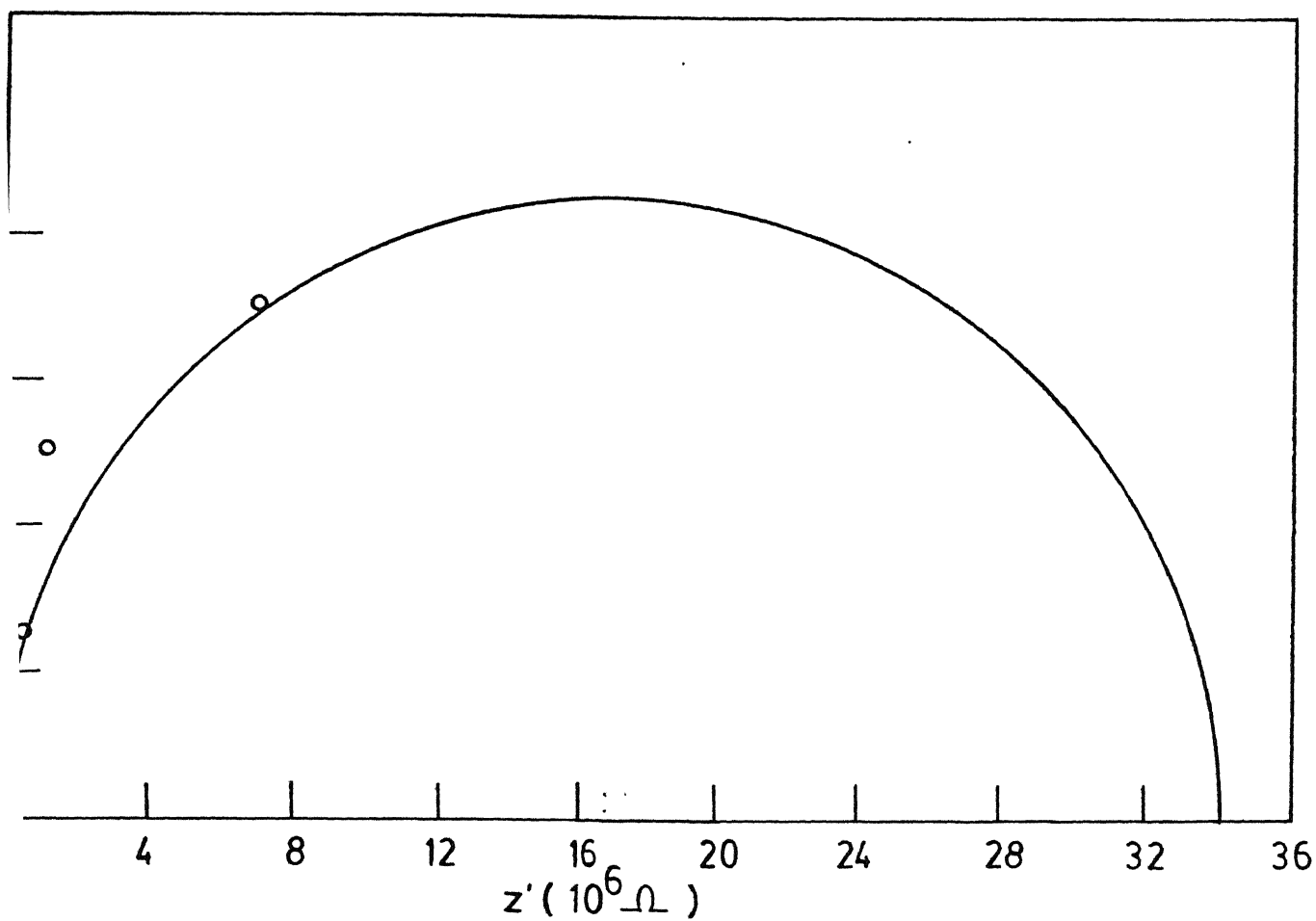


FIG. 3.7

COMPLEX IMPEDANCE PLOT FOR GLASS
SYSTEM IA₁



3.8 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM A₂
(T = 204 °C)

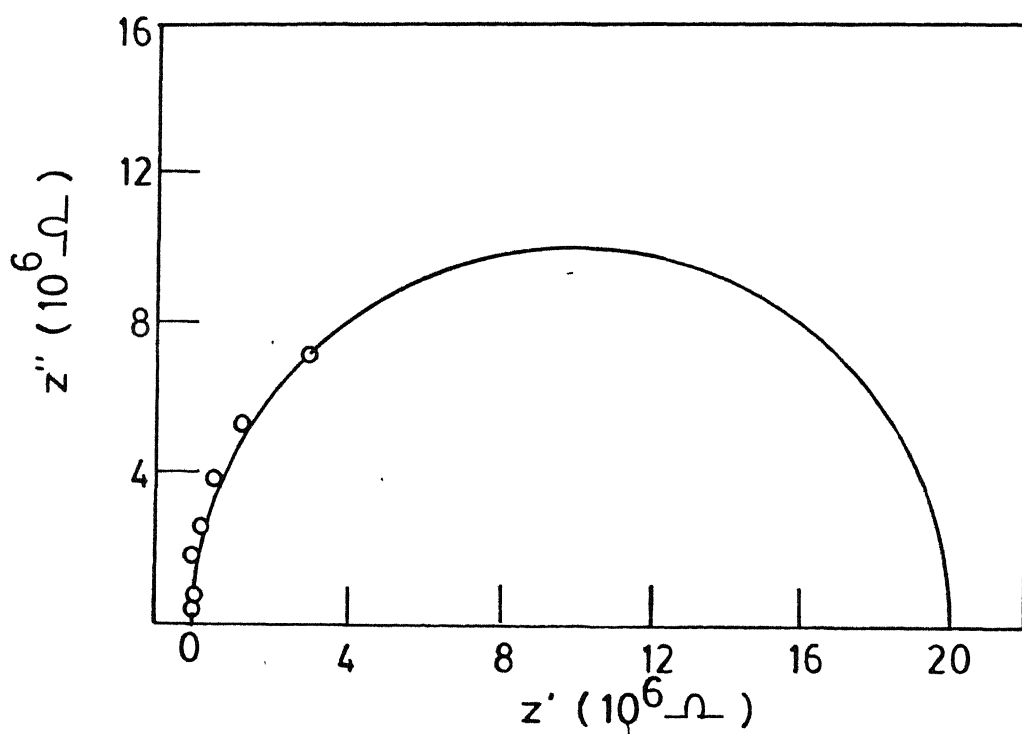


FIG.3.9 COMPLEX IMPEDANCE PLOT FOR GLASS
SYSTEM IA_2 (2 hrs I E WITH Cu)
($T = 139^\circ C$)

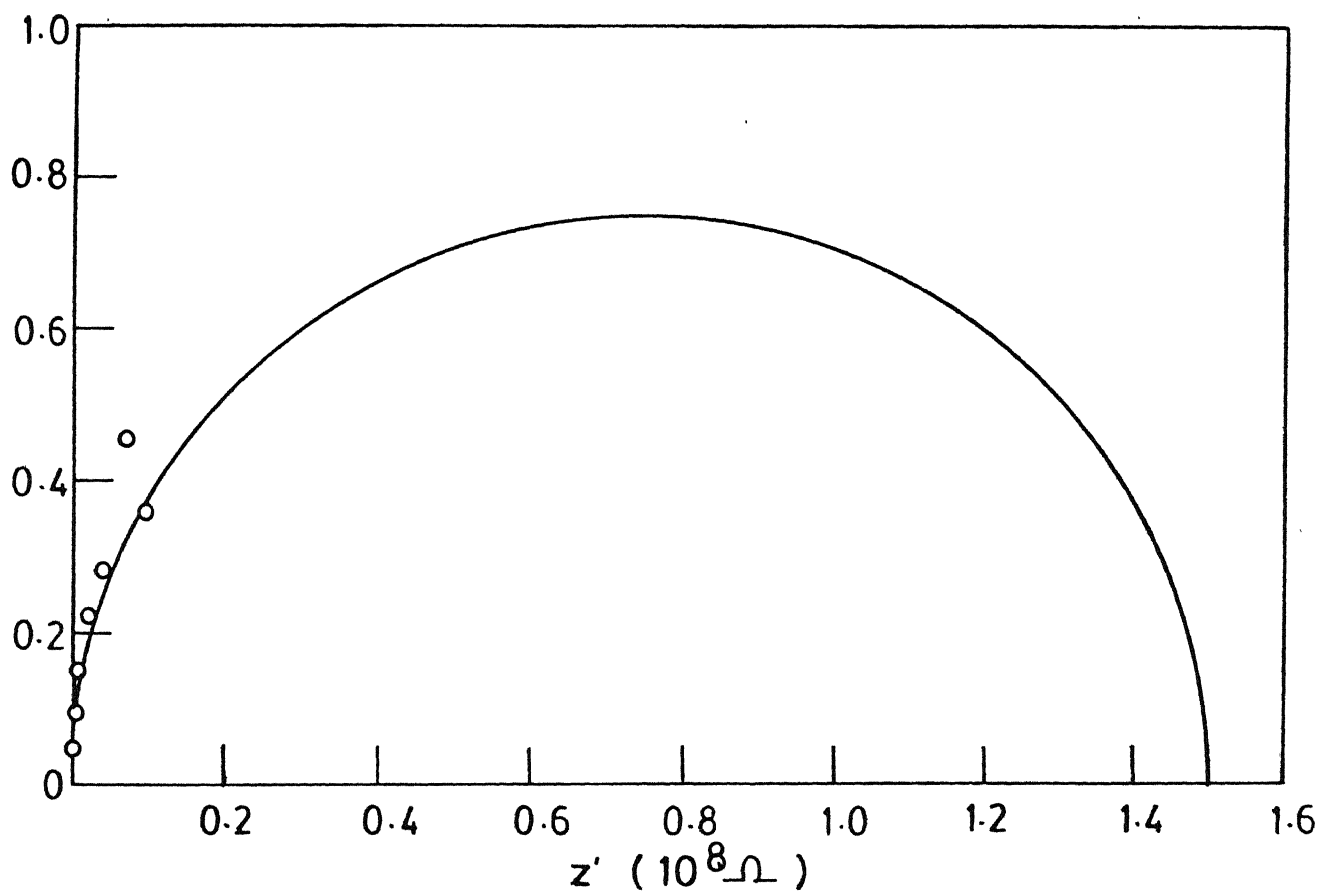


FIG. 3.10 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM
IA₂ (12 hrs I.E. WITH Cu) T = 139°C

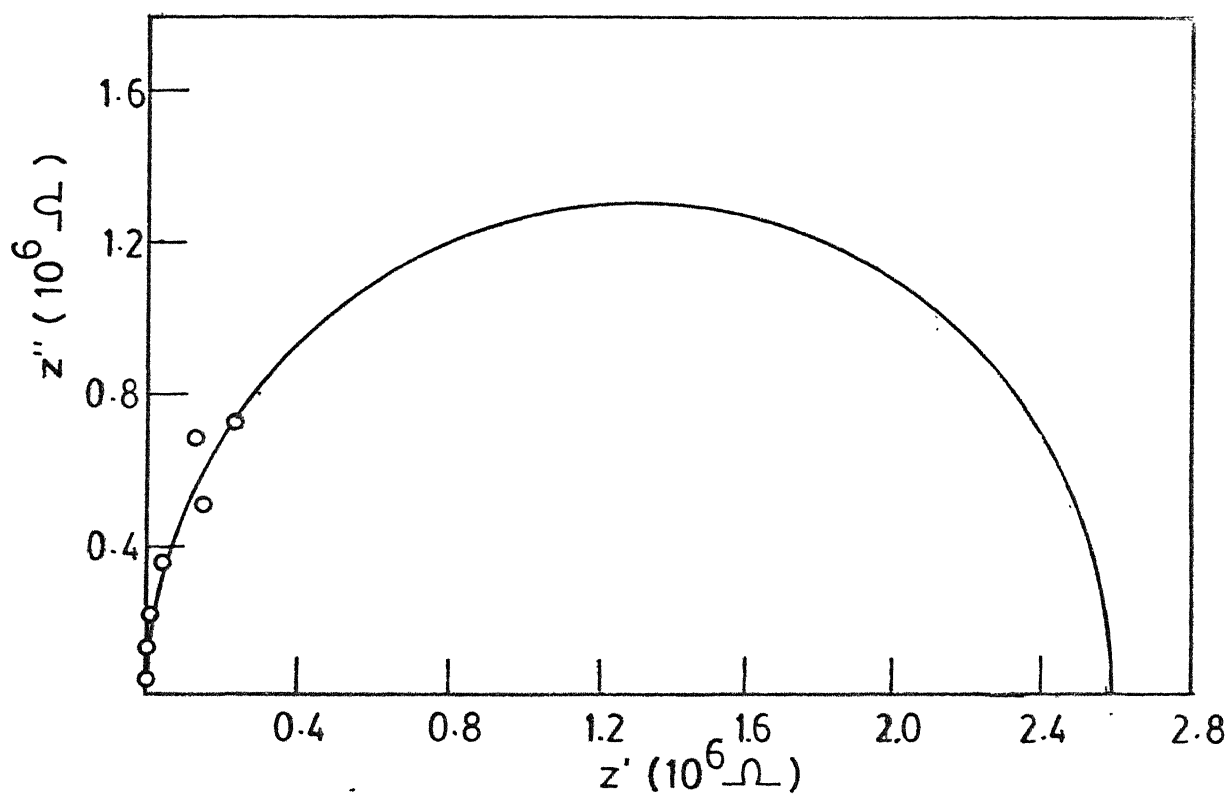


FIG. 3.11 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM
1A₂ (1E WITH Ag) T=125°C

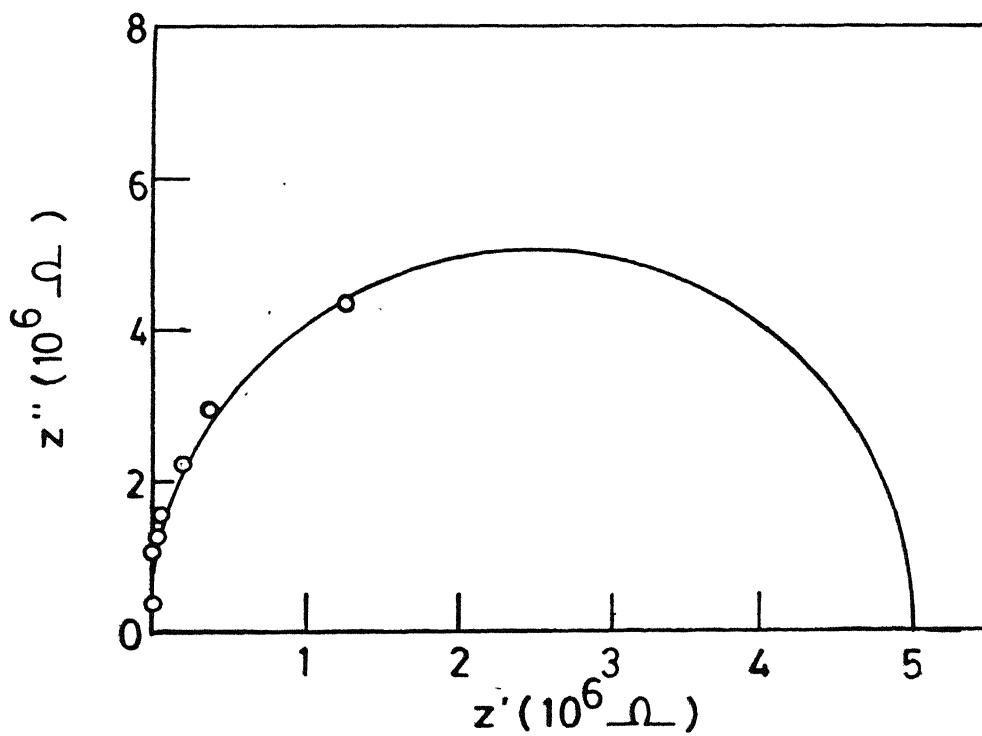


FIG. 3.12 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM A₃ (T = 123.5°C)

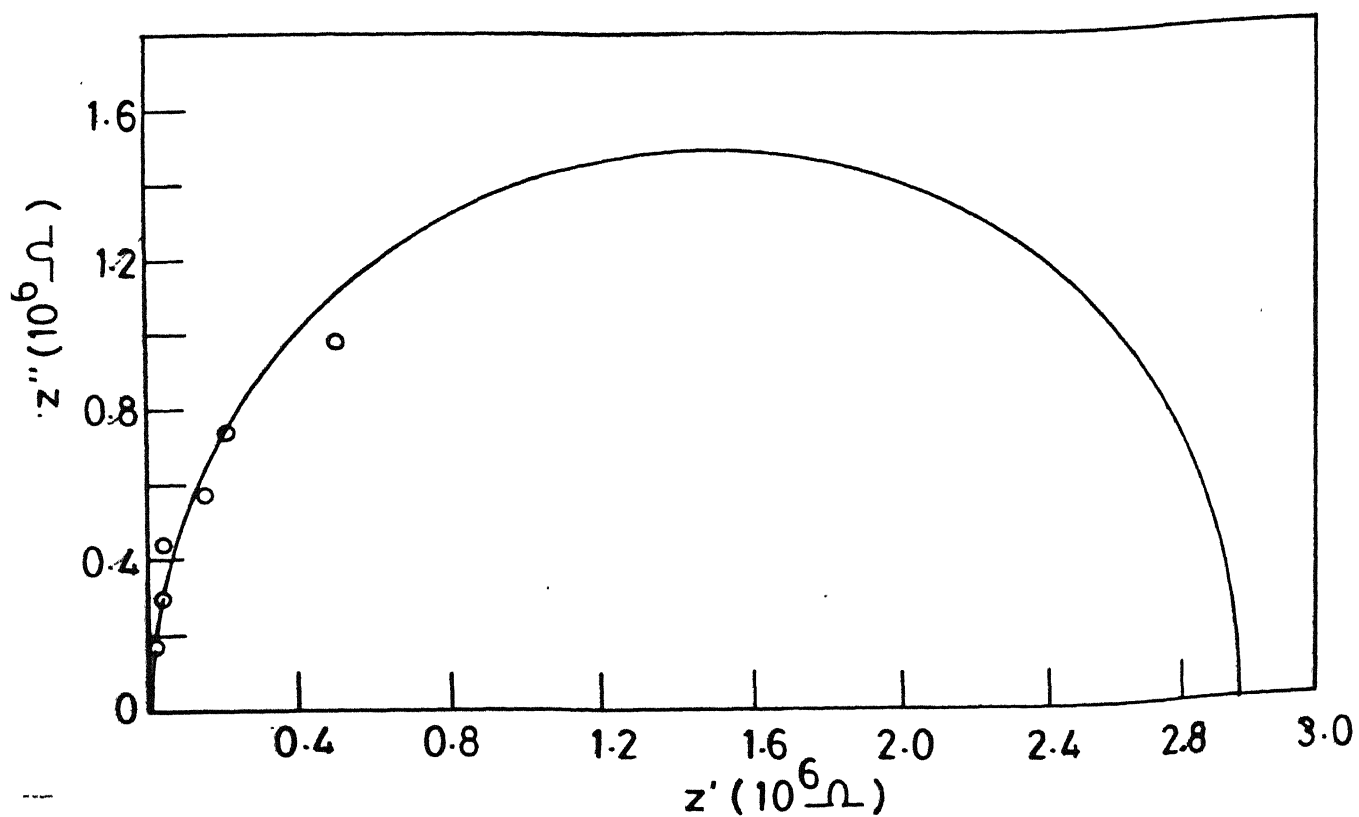


FIG.3.13 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM
1A₃ (12 hrs I E with Cu) T=139°C

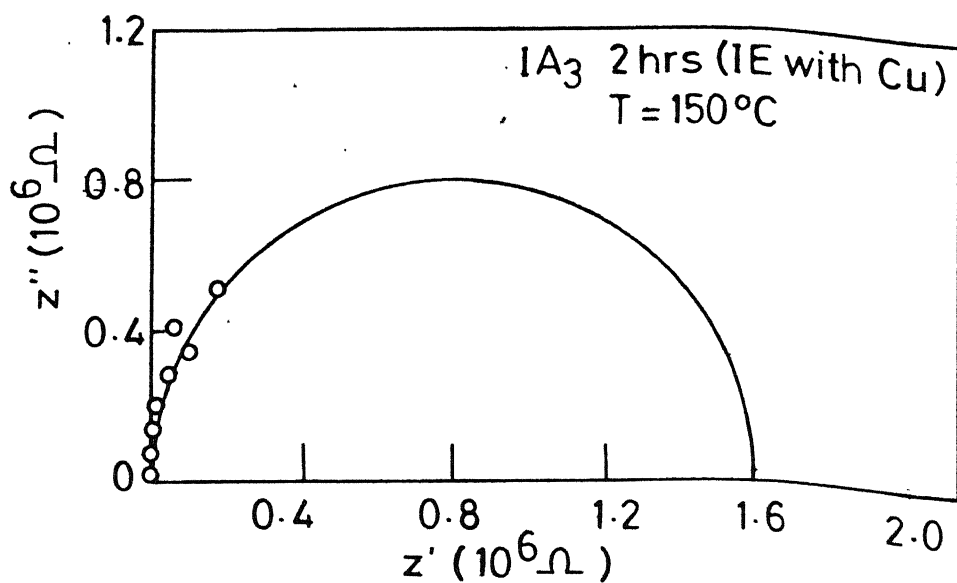


FIG. 3.14

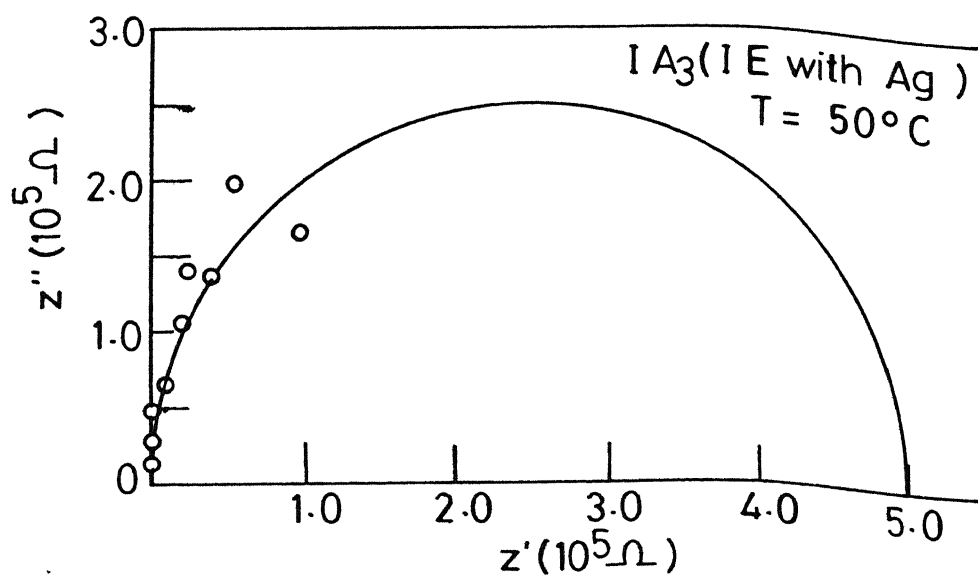


FIG. 3.15

COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM

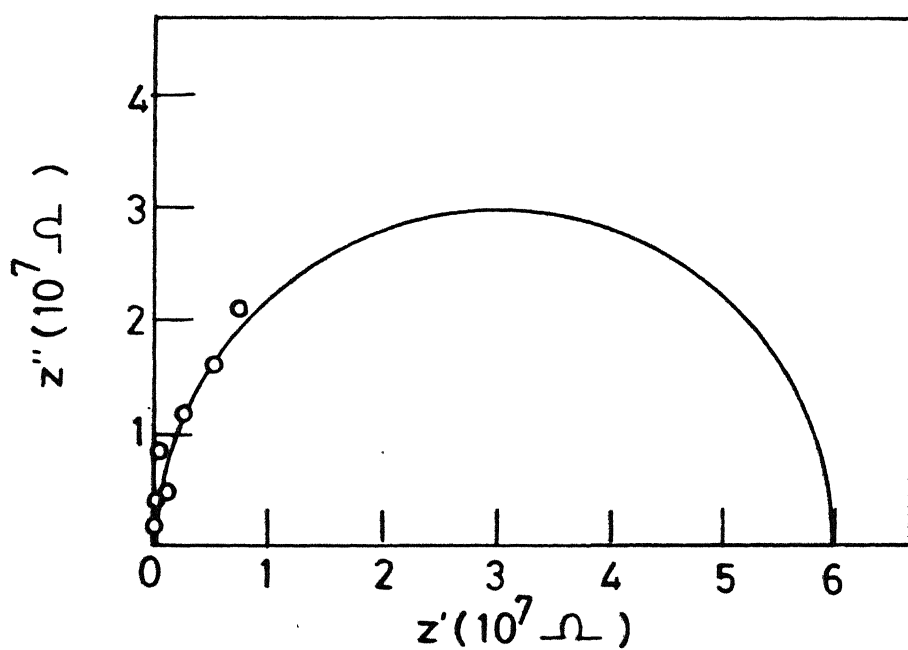


FIG. 3.16 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM A₄ (T = 181°C)

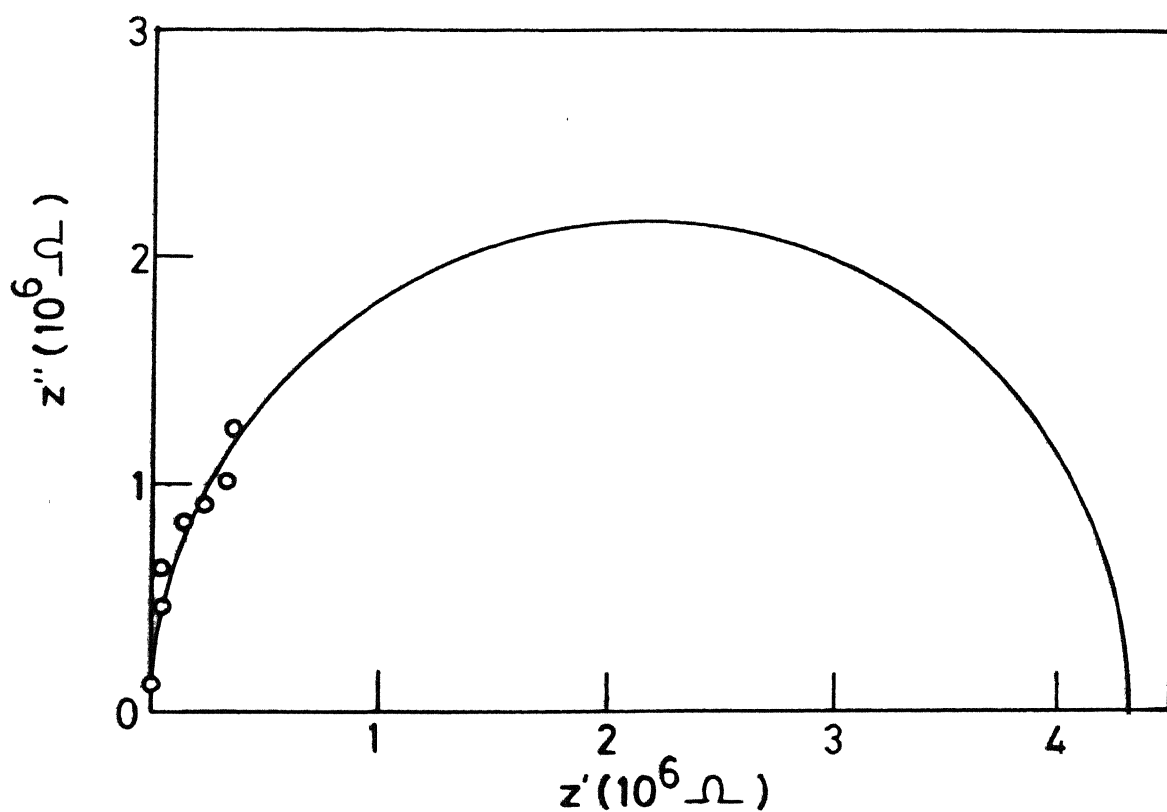


FIG.3.17 COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM
1A₄ (IE with Ag), T= 97°C

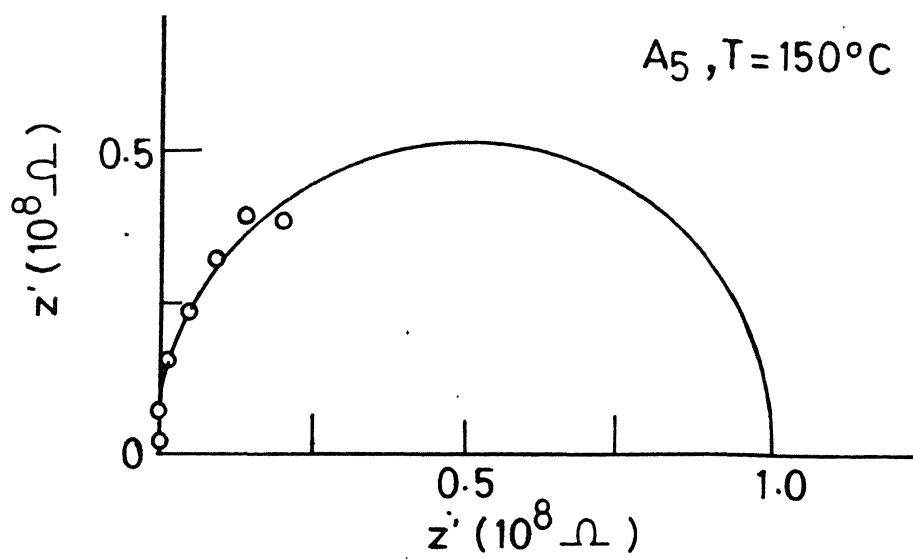


FIG. 3-18

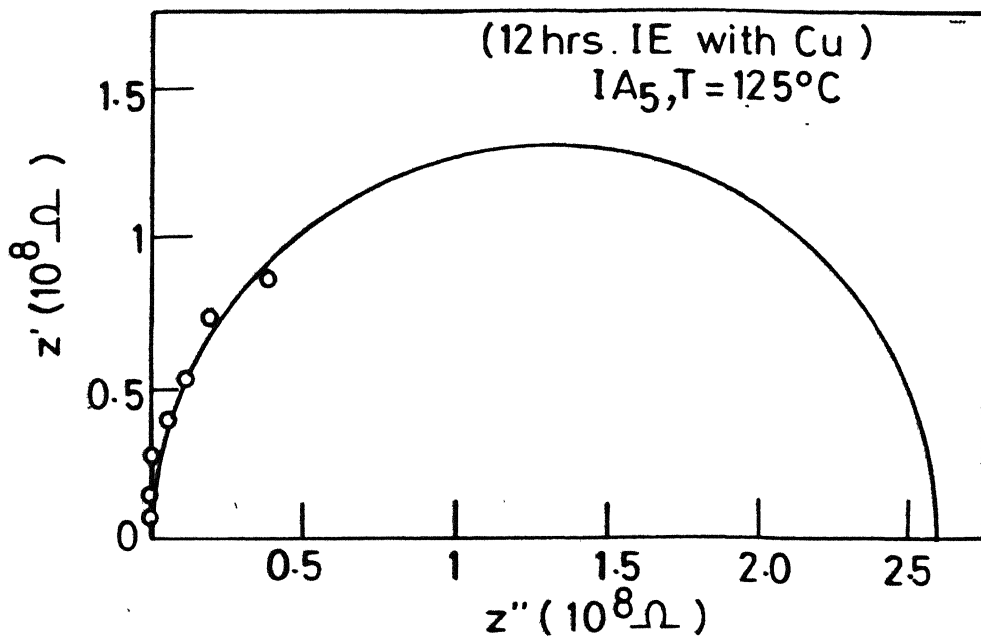


FIG. 3-19

COMPLEX IMPEDANCE PLOT FOR GLASS SYSTEM

The typical switching behaviour (I-V plots) of an ion-exchanged glass system (IA) to high conducting glass (HIA) system has been shown in Figs. 3.20 to 3.23. In these figures both IA state and HIA state are shown. These plots are characterized by negative resistance region shown by arrows in these figures. High conducting state is stable and HIA glass systems are new materials characterized by high conductivity. Variation of threshold field with temperature for IA glass systems are shown in Fig. 3.24.

Figs. 3.25 to 3.29 show the variation of $\log \rho$ with $1/T$ for virgin (A) ion-exchanged (IA) and high conducting (HIA) glass systems.

The temperature dependence of resistivity is found to obey the Rasch-Hinrichsen equation

$$\rho = \rho_0 \exp \left(\frac{Q}{KT} \right) \quad (3.3)$$

where

ρ : resistivity of the sample

ρ_0 : pre-exponential factor

Q : activation energy for conduction

K : Boltzman constant

T : temperature

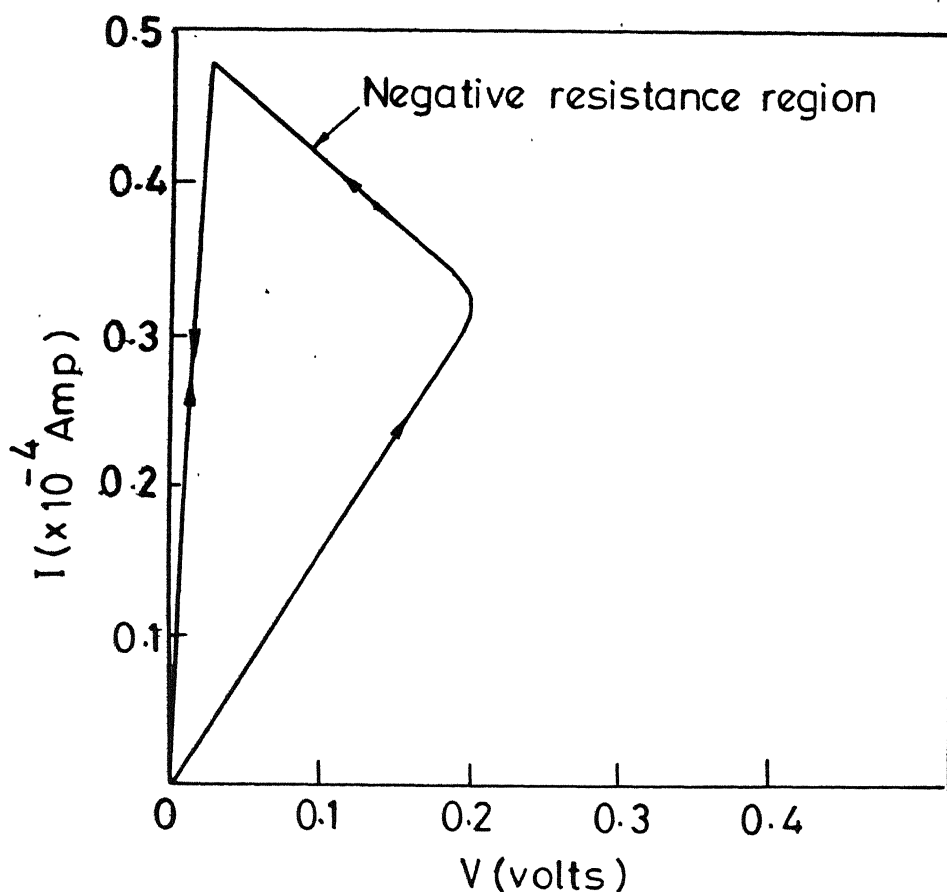


FIG.3.20 SWITCHING OF GLASS SYSTEM IA_1 (IE with AG) to HIA_1 GLASS SYSTEM. $T_c = 232^\circ C$

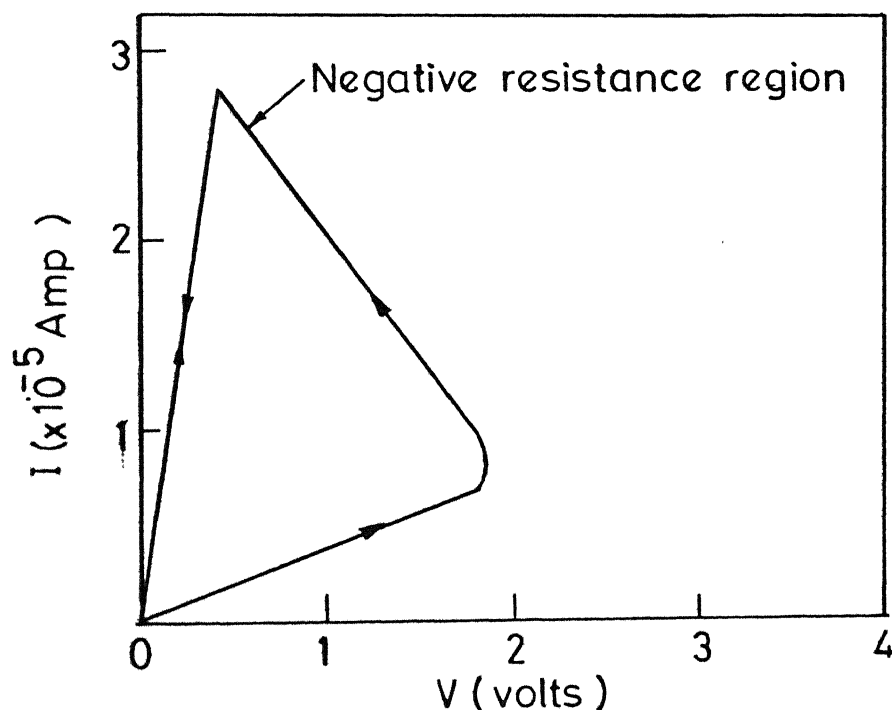


FIG.3.21 SWITCHING OF GLASS SYSTEM IA (IE with AG) AT $177^\circ C$ to HIA_2 GLASS SYSTEM. $T_c = 177^\circ C$

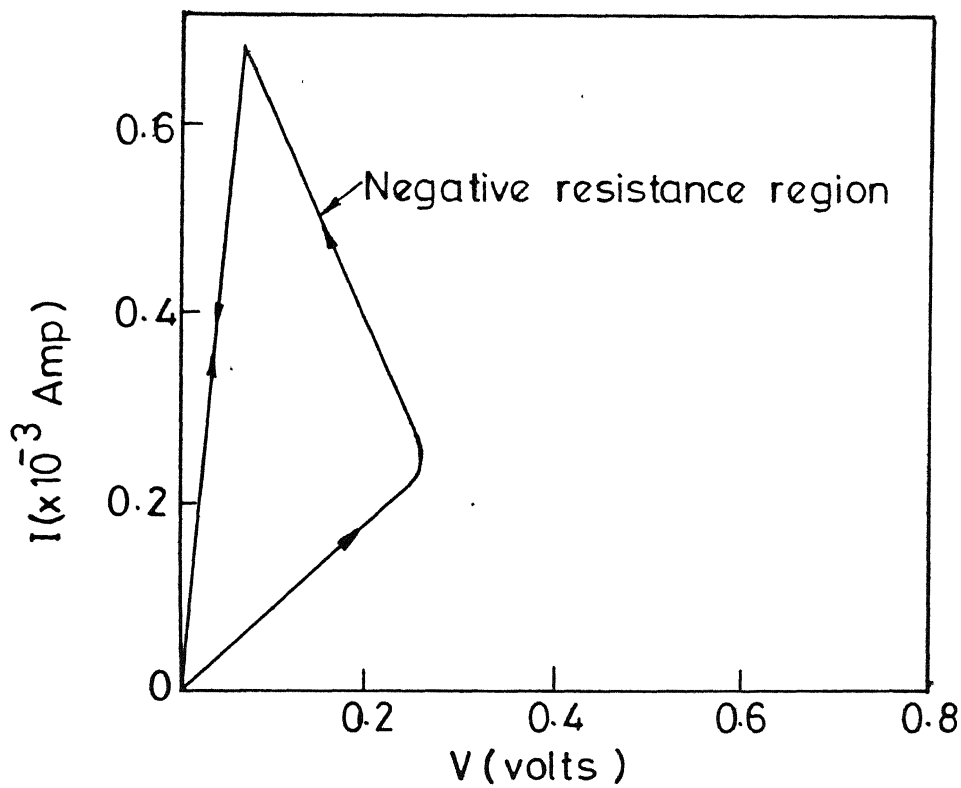


FIG. 3.22 SWITCHING OF GLASS SYSTEM IA_3 (IE with AG) TO HIA_3 GLASS SYSTEM $T_c = 264^\circ\text{C}$

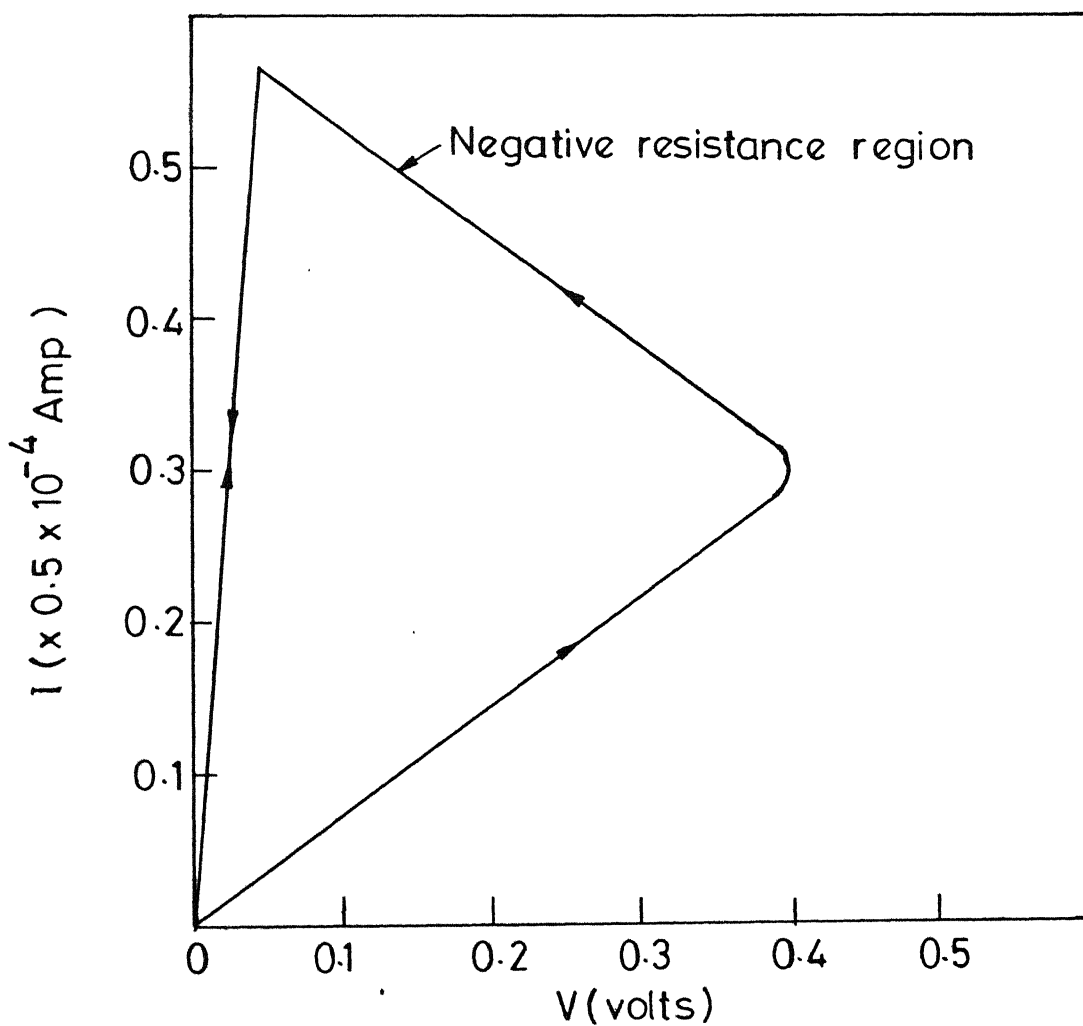


FIG. 3.23 SWITCHING OF GLASS SYSTEM IA_4 (IE with AG) TO HIA_4 GLASS SYSTEM $T_c = 259^\circ\text{C}$

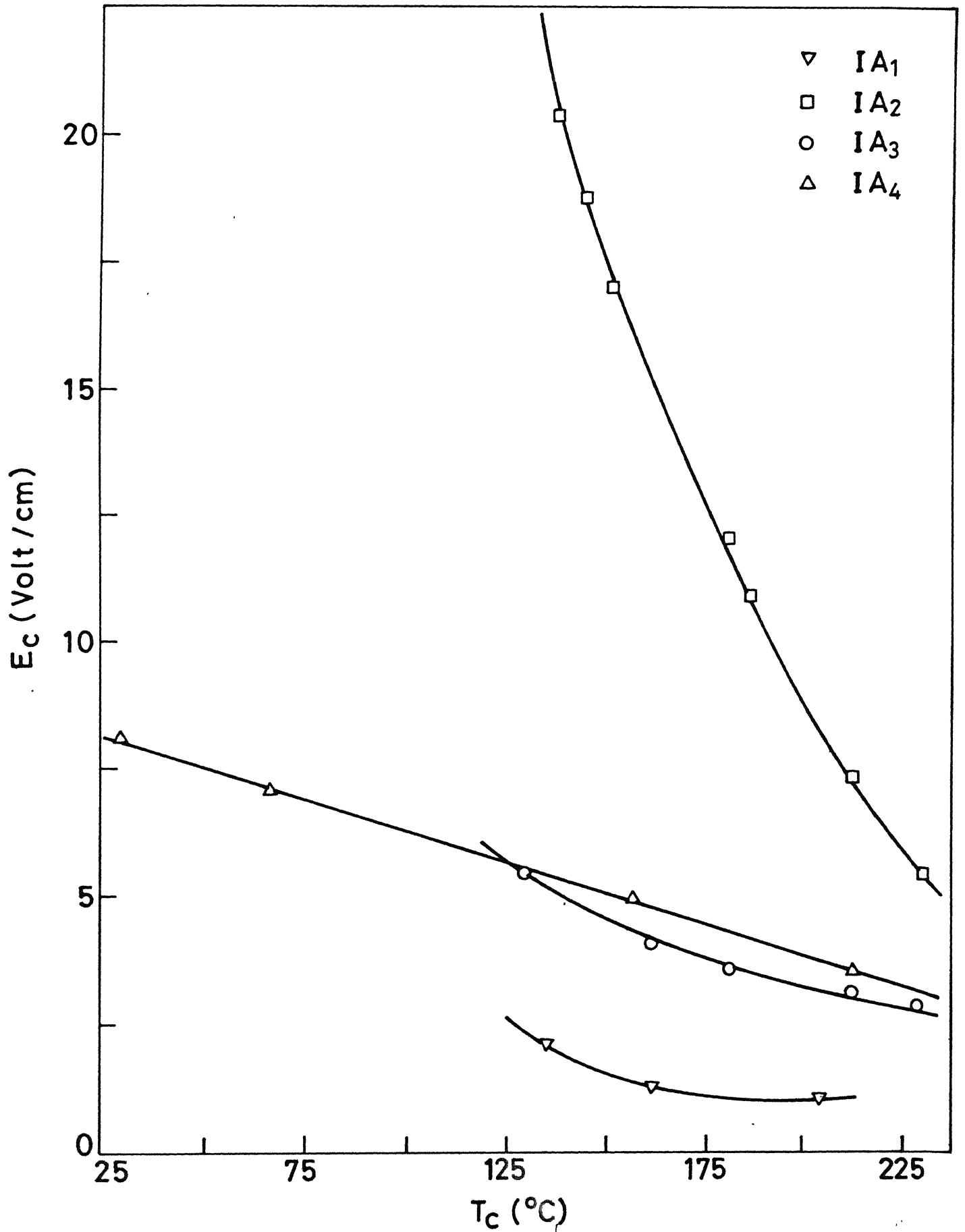


Fig. 3.24 Temperature variation of critical electric field (E_c) for glass system IA (I.E. with Ag).

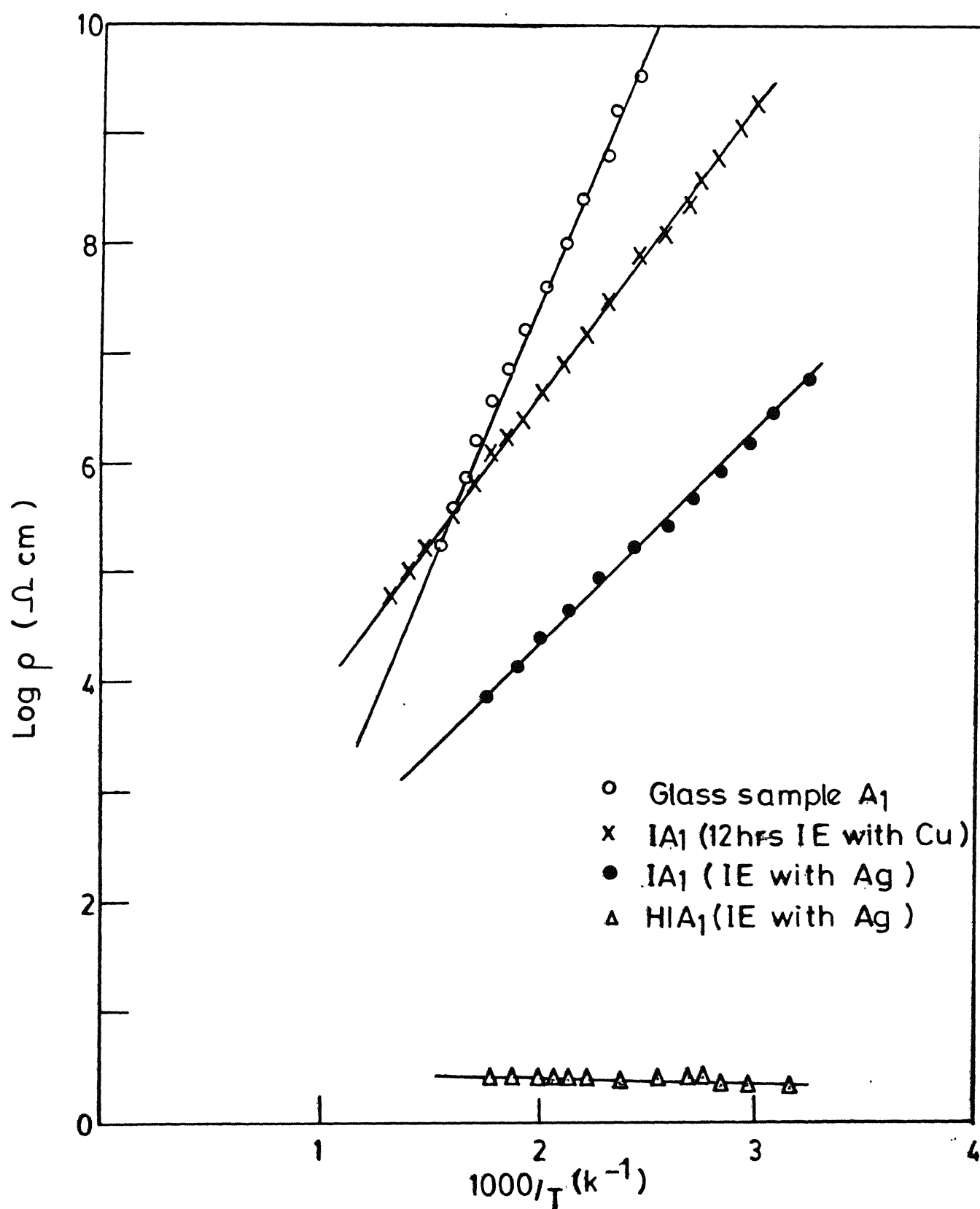


FIG. 3.25 TEMPERATURE VARIATION OF D.C. RESISTIVITY FOR GLASS SYSTEMS. A₁, IA₁ AND HIA₁

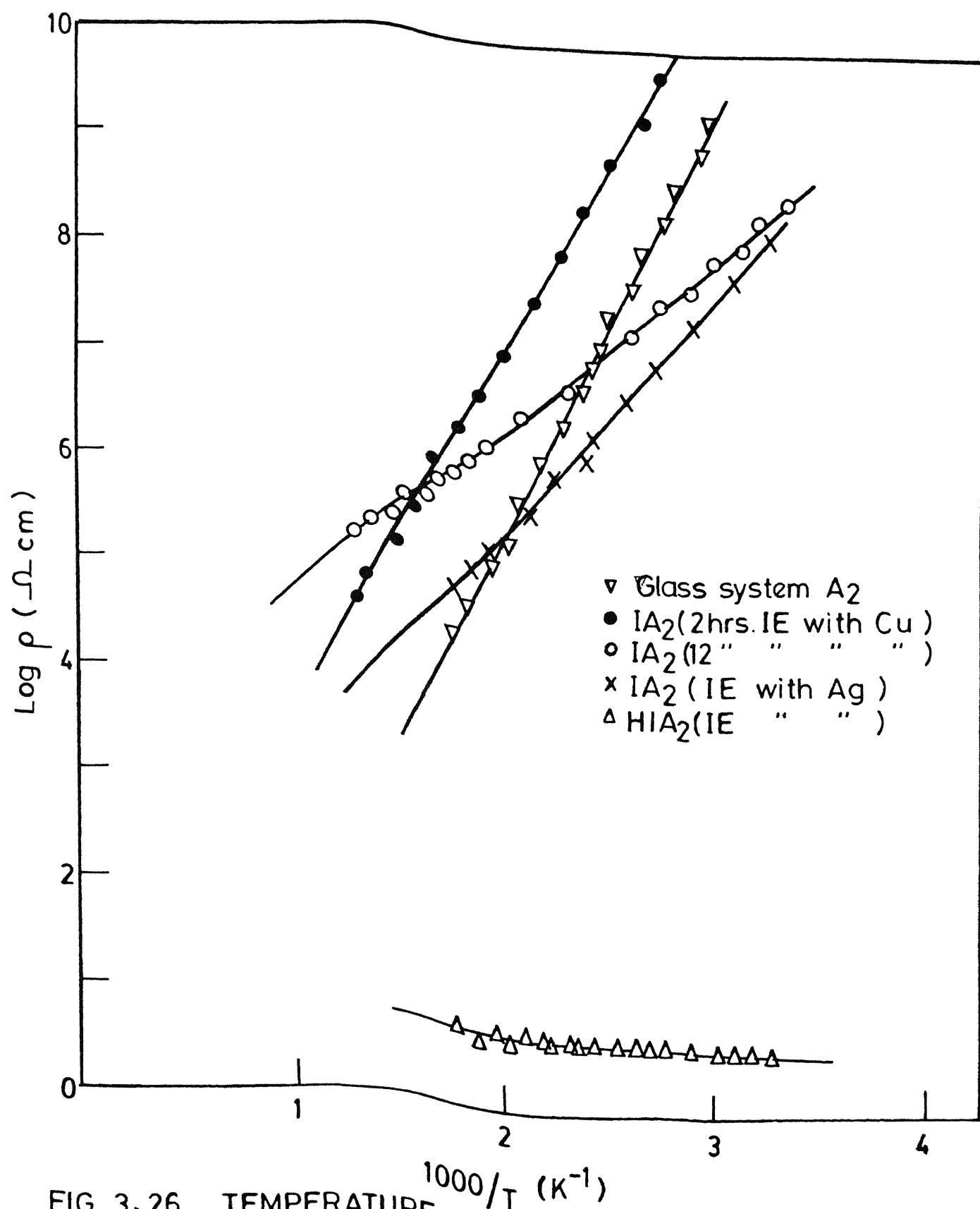


FIG. 3.26 TEMPERATURE VARIATION OF D.C. RESISTIVITY FOR GLASS SYSTEMS A₂, IA₂ AND HIA₂

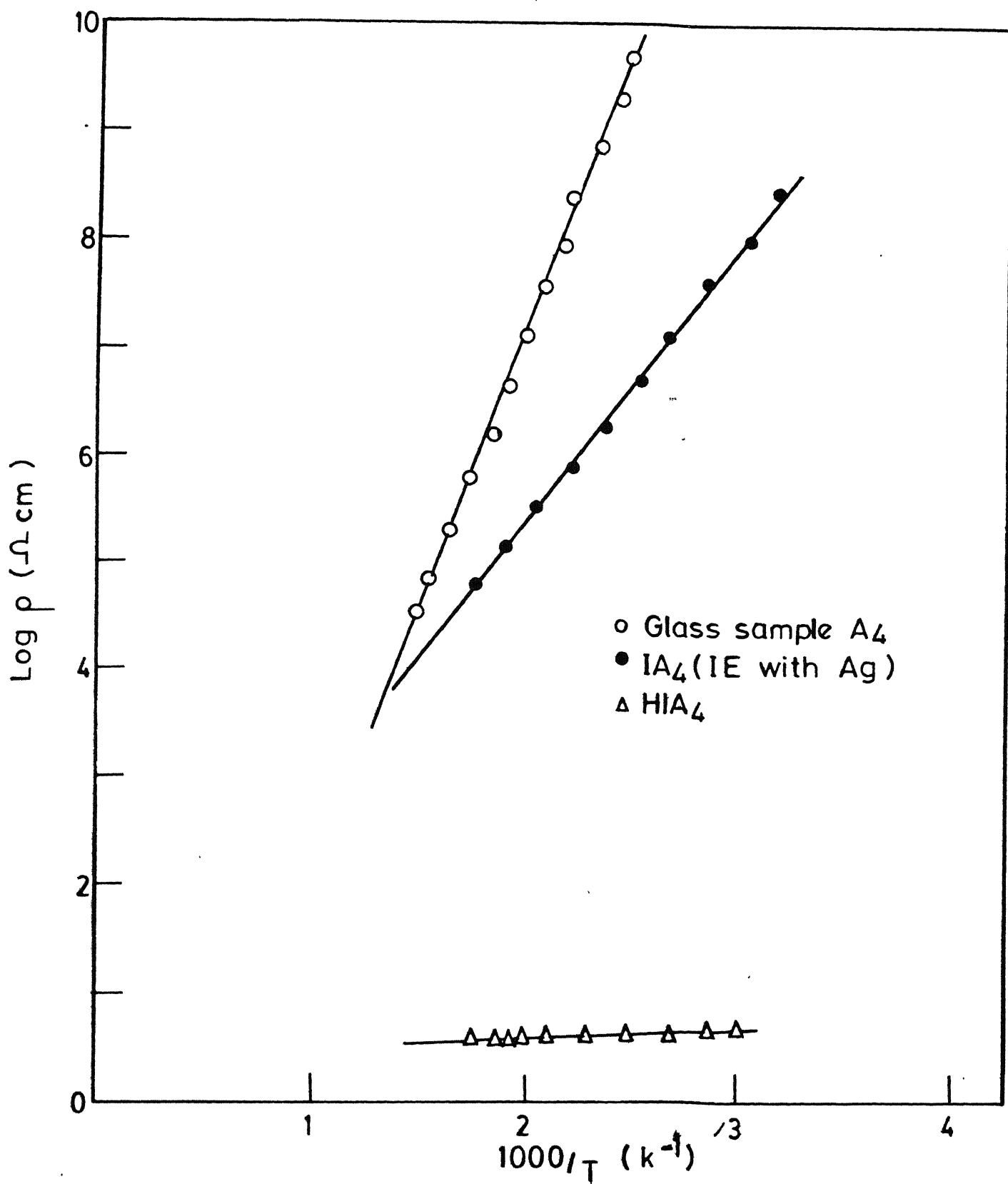


FIG. 3.28 TEMPERATURE VARIATION OF D.C. RESISTIVITY FOR GLASS SYSTEMS A₄, IA₄ AND HIA₄

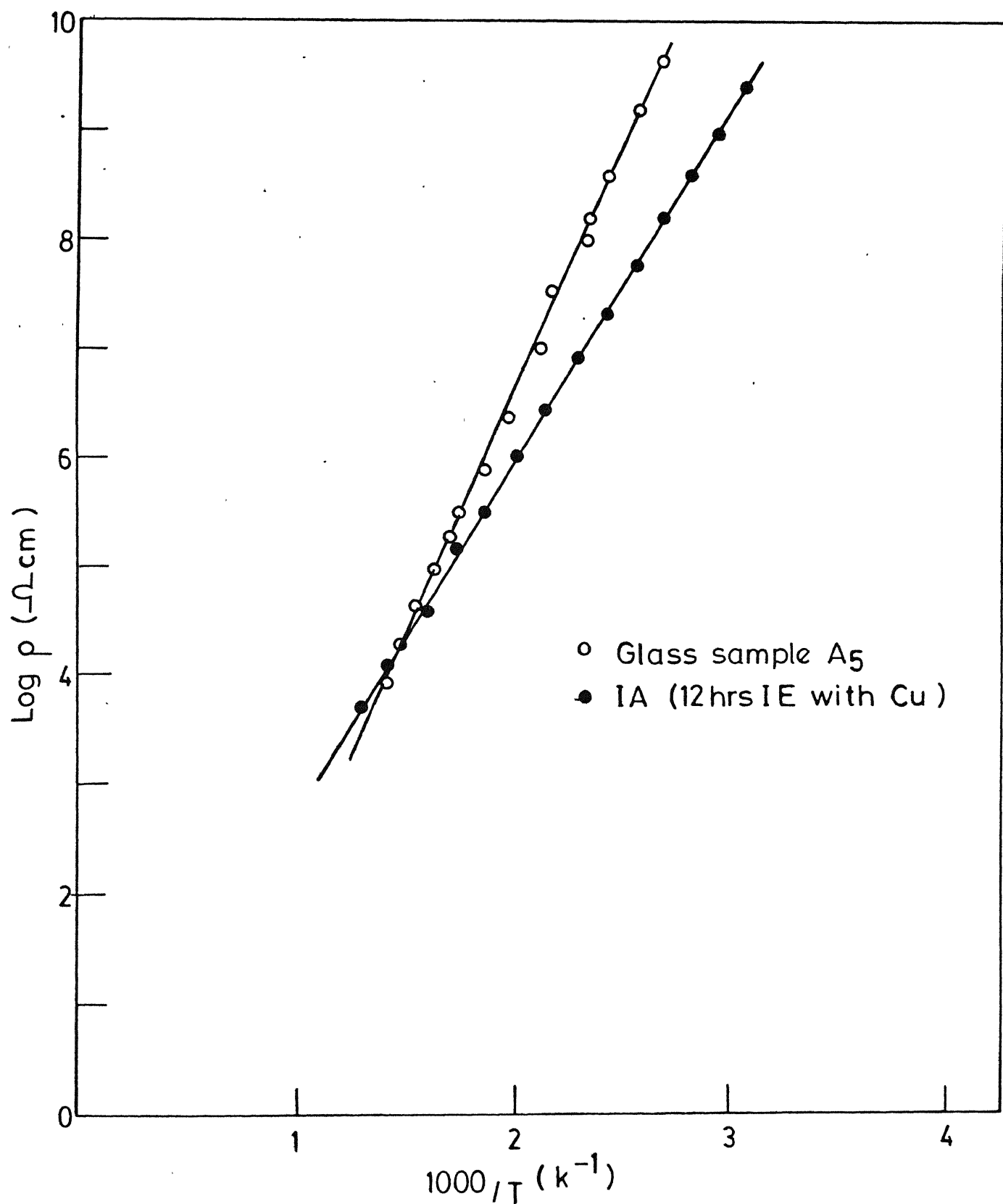


FIG. 3.29 TEMPERATURE VARIATION OF D.C. RESISTIVITY FOR GLASS SYSTEMS. A₅ AND IA₅

Table 3.3 Activation Energy (Q) and Pre-exponential factor (ρ_0)

Glass System	A Non-Ion exchanged	I A 2 hrs. I.E. with C_u	I A 12 hrs. I.E. with C_u	I A I.E. with A_g	HIA I.E. with A_g
1	ρ_0 6.30×10^{-3}		19.95	2.51	3.16
	Q 0.88		0.48	0.36	0.01
2	ρ_0 1.41×10^{-3}	0.56	7.94	7.94	6.30
	Q 0.76	0.69	0.31	0.42	0.02
3	ρ_0 4.46×10^{-4}	0.39	0.12	0.15	14.12
	Q 0.75	0.54	0.44	0.42	0.02
4	ρ_0 1.0×10^{-3}			3.16	2.51
	Q 0.96			0.44	0.01
5	ρ_0 5.62×10^{-3}		0.31		
	Q 0.88		0.57		

Units : ρ_0 : Ohm-cm

Q : eV

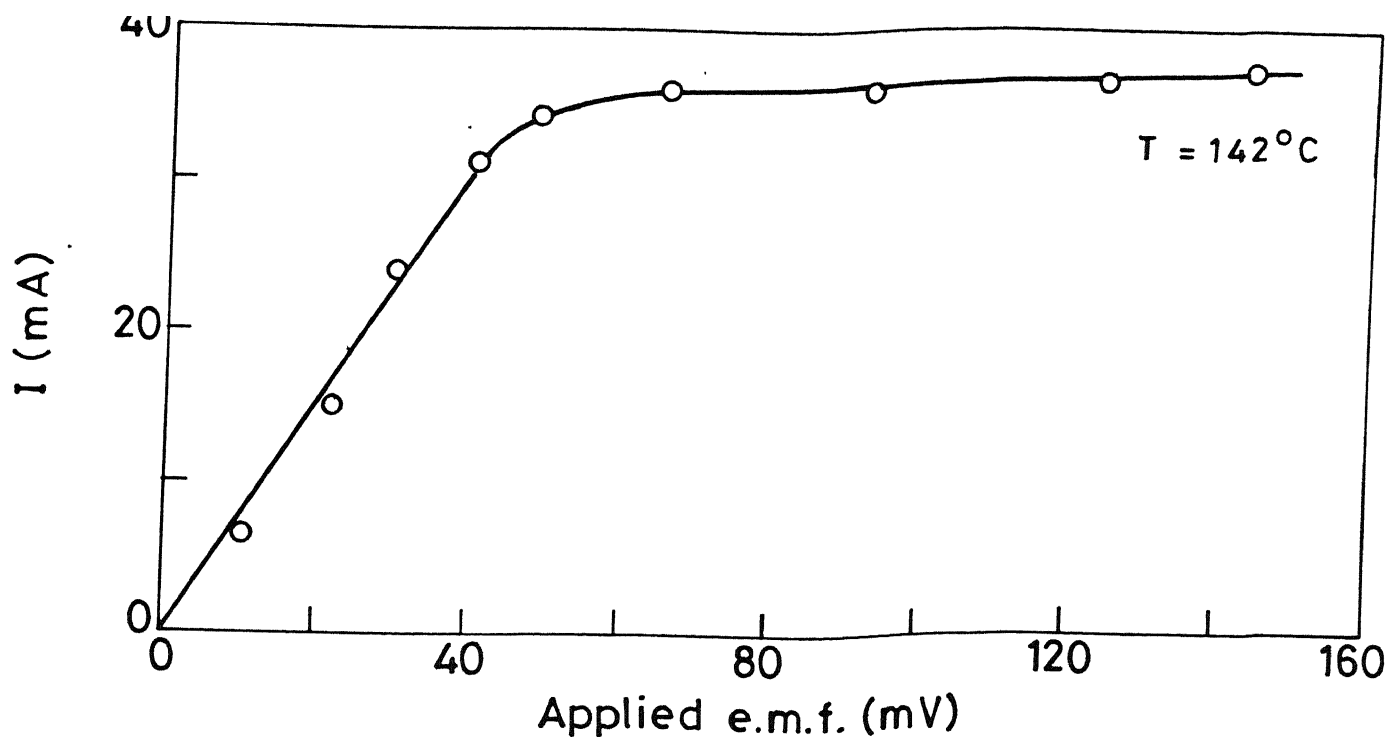


Fig. 3.30(a) Steady state current voltage curves for the polarization cell $\text{Ag}/\text{HIA}_1/\text{C}^+$.

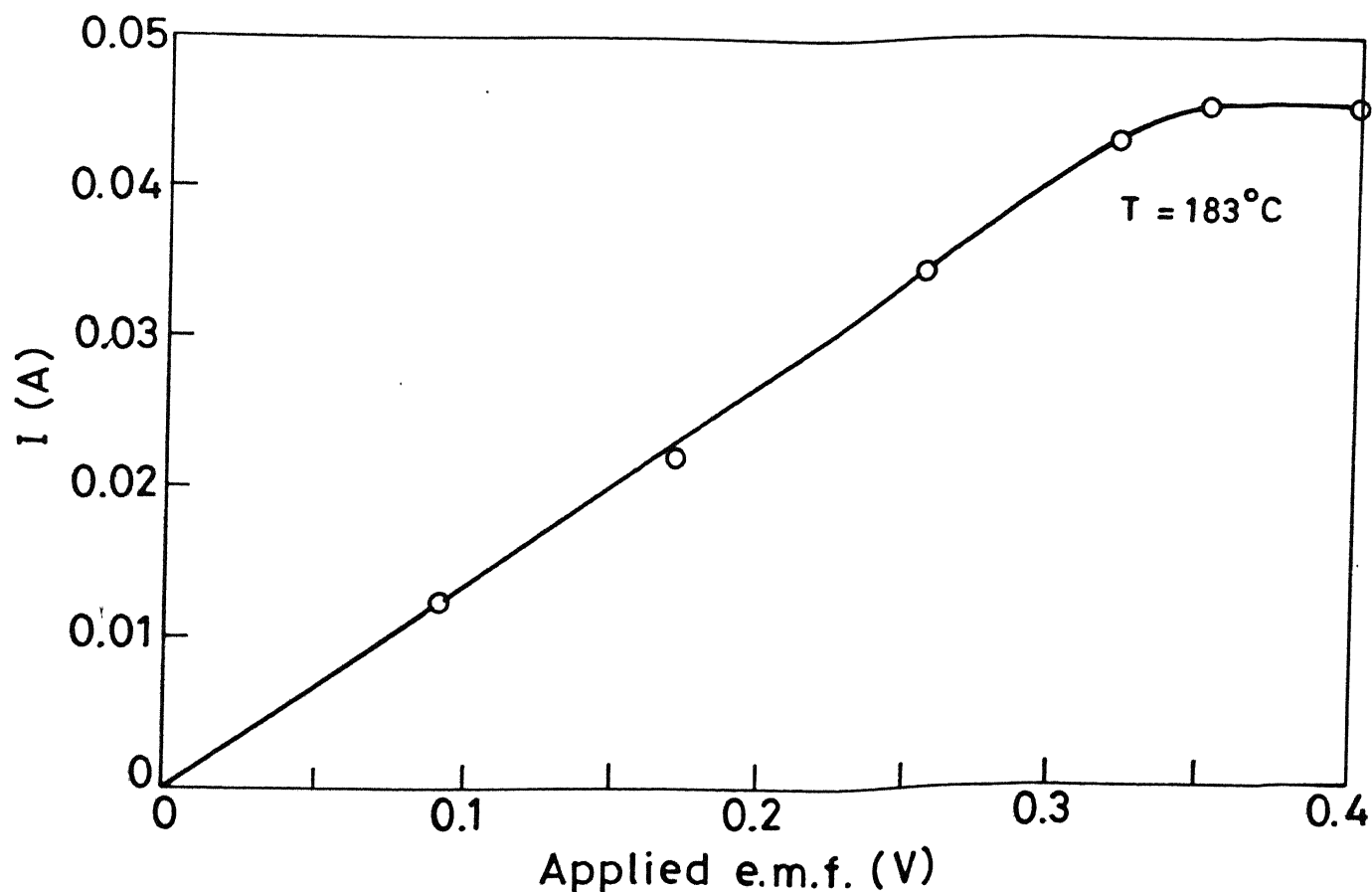


Fig. 3.30(b) Steady state current voltage curves for the polarization cell $\text{Ag}/\text{HIA}_2/\text{C}^+$.

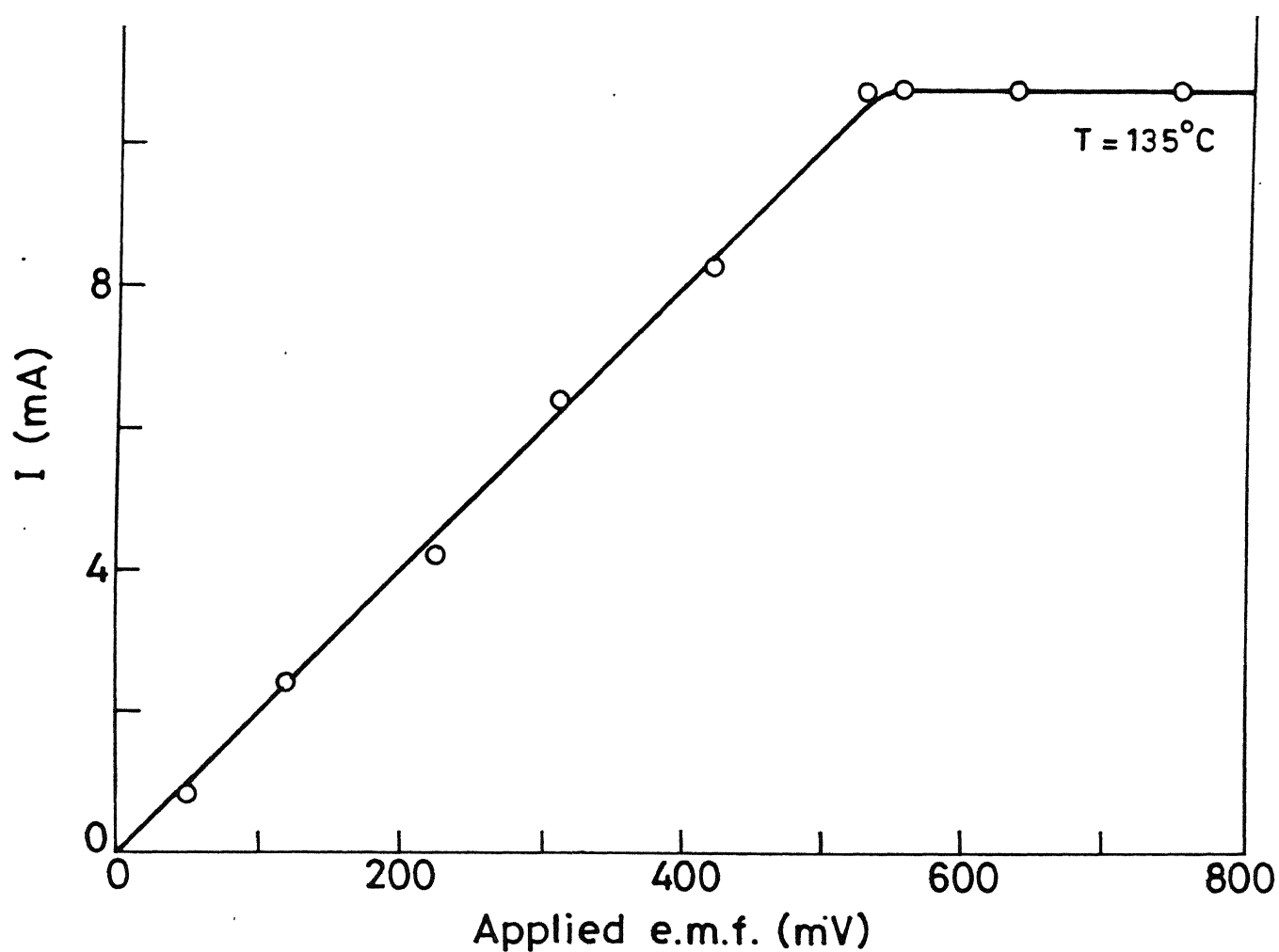


Fig.3.30(c) Steady state current voltage curves for polarization cell $\text{Ag}/\text{HIA}_3/\text{C}^+$

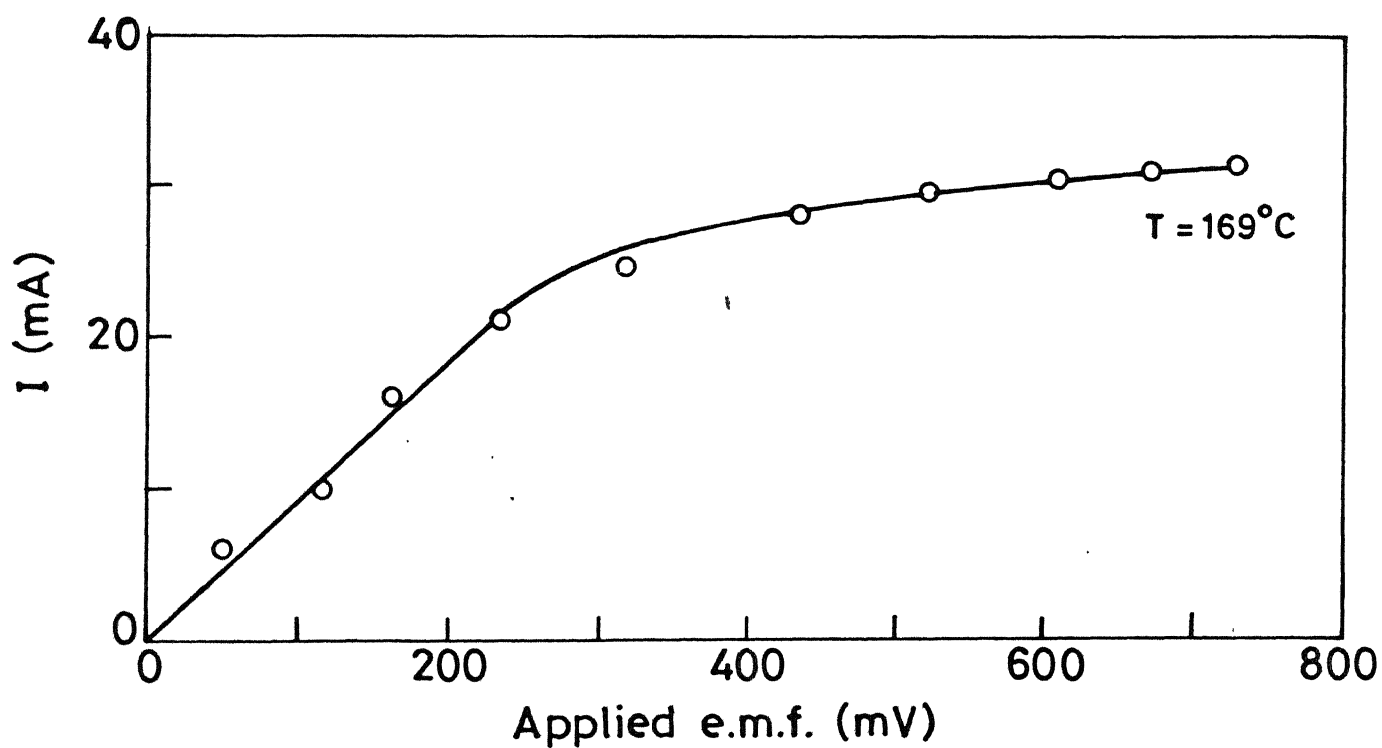


Fig. 3.30 (d) Steady state current voltage curves for the polarization cell $\text{Ag}/\text{HIA}_4/\text{C}^+$

These holes are surrounded by non-bridging oxygens (NBO) which act as host for the cations. As it has been already discussed in Section 1.2, the conductivity has Arrhenius like temperature dependence given by (Rawson 1984)

$$\sigma = \sigma_0 \exp(-Q/KT)$$

The ionic conductivity increases with increase of alkali oxide concentration but this increase is nonlinear (Rawson H 1984). The activation energy decreases with increase in the alkali metal ion concentration.

Ion-exchanged glass system shows a decrease in resistivity and activation energy. This has been explained on the basis of ionic radii of sodium ion and silver ion respectively. If the glass is sufficiently open which is the case when enough alkali ions are present (valid in our glass system) the contribution due to elastic distortion of the glass structure (mechanical energy) to the activation energy can be neglected. In such a situation, the larger ions (silver in this case) should have lower activation energies.

Switching behaviour can be explained on the assumption that the ion-exchanged layer consists of an interconnected silver deficient phase and a silver rich layer with broken interconnectivity. Permanent gain of the ion-exchanged samples to

the highly conducting state under influence of a suitable combination of electric field and temperature is believed to arise due to the formation of links between the disjointed portions of the silver rich phase.

Fig. 3.30 gives the steady state current-voltage characteristics for the polarization cell Ag/HIA/C^+ . From these curves it seems that the conductivity in the high conducting state is ionic in nature.

CHAPTER 4

CONCLUSION

From the present investigations about electrical properties of alkali containing oxide glasses, following conclusions are drawn.

- 1) A.C. and D.C. electrical conductivity measurements may be made on these glasses, using silver paint as non blocking electrodes. Non ion-exchanged glasses show ionic conductivity in which sodium ions are the charge carriers. The resistivity level is quite high ($\approx 10^9 \Omega \text{cm}$) at room temperature. The activation energy is about 0.8 eV. Conductivity increases with increasing amount of sodium concentration.
- 2) Ion exchanged glasses show an improvement by about two orders of magnitude in electrical conductivity as compared to that of the virgin glasses. The activation energy comes down to around 0.4 eV. The maximum conductivity of $10^{-6} (\Omega \text{cm})^{-1}$ at room temperature may be achieved by the ion-exchange process.
- 3) The charge carrier mechanism in ion-exchanged glasses is the migration of silver (or copper) ions.

- 4) It has been established that an optimum combination of electric field and temperature brings a permanent increase of conductivity by many orders of magnitudes. These electric fields are found to be quite low of the order of 2 Volt/cm. With increasing temperature the value of critical electrical field decreases. The initial glass composition too influences this critical electric-field.
- 5) The activation energies in the high conducting state are very small, in some cases they tend to be negligibly small becoming almost zero. The highest conductivity of the order of $10^{-2} (\Omega\text{cm})^{-1}$ may be achieved in this high conducting state.

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